

AN ELECTRON SPIN RESONANCE STUDY OF  
n-DOPED TCNQ AND 2:1 TCNQ COMPLEX SALTS

Stefan Alan Nyarady

RARI  
AL POSTGRADUATE SCHOOL  
TEREY, CALIF. 93940

# NAVAL POSTGRADUATE SCHOOL

## Monterey, California



# THESIS

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by

Stefan Alan Nyarady

Thesis Advisor:

William M. Tolles

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by

Stefan Alan Nyarady  
Ensign, United States Navy  
B.S., Stanford University, 1972

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## ABSTRACT

Complex 2:1 TCNQ salts of quinoline, 2-methylquinoline, 4-methylquinoline, and 7-methylquinoline were made. Their ESR spectra were observed and their magnetic susceptibilities and resistivities were determined. A new donor, 1,4-dimethyl-1,4-dihydro-s-tetrazine(DMDHT), was tried with TCNQ as acceptor. Magnetic susceptibility, resistivity, and ESR g-value measurements were made on the resulting complex. A complex of  $\text{DMDHT}^+/\text{C}_{10}\text{N}_4^-$  was made and an intense ESR singlet was observed.

TCNQ crystals doped with DMDHT resulted from attempts to make the  $\text{DMDHT}^+(\text{TCNQ})_2^-$  complex salt. Resistivity measurements showed these crystals to be  $10^3$  times more conducting than extremely pure TCNQ. Variable temperature studies showed an activation energy for conduction of 0.55 eV for both the doped and undoped TCNQ.

The ESR absorption of doped TCNQ was relatively constant from 350°K to 100°K. A possible explanation for this observed behavior is an excited state triplet 0.02 eV above the valence band of TCNQ. The lack of an observed doublet is explained with the "almost-localized" electron model.

As ESR kinetic study of the high temperature decomposition of TCNQ indicated more than one species resulting from decomposition.





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## 1. INTRODUCTION

Semiconducting behavior in organic solids was first reported at the turn of the century [Ref. 1]. It was not until fifty years later however that active interest in organic semiconductors began. Recent activity can be traced to Mulliken's theoretical analysis of charge transfer compounds in 1952 [Ref. 2]. An investigation of the electrical properties of organic material was a natural extension of the thorough understanding of semiconductivity in inorganic materials. Some of the concepts concerning inorganic semiconductors are instructive although not completely applicable when dealing with organic semiconductors.

The main problem in the study of organic semiconductors is understanding how electric charge enters and is transported through a molecular solid, since the distances involved are large on a molecular scale. Much of the recent work has been of a theoretical nature in an effort to shed light on this topic [Refs. 3, 4, and 5]. An important reason for interest in radical-ion salts and charge transfer complexes is that in the solid state many of these compounds show non-ionic electrical conduction, offering a unique opportunity to study electron conduction and interaction in solids [Ref. 6]. The great variety of organic compounds and their physical properties offer promise of extending the scope of organic semiconductors far beyond that available in the two commercially important semiconductors, silicon and germanium. Recent interest in organic semiconductors is tied to the intriguing possibility of tailoring an organic compound with some desired electrical properties, once they are understood well enough.





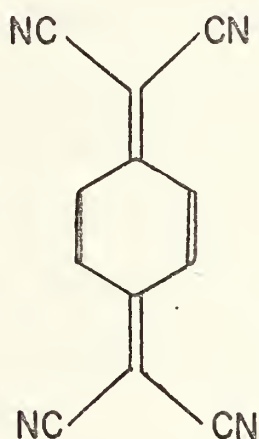
Despite interest over the past few decades, relatively few organic solids have been found with an electrical resistivity of less than  $10^4$  ohm-cm [Ref. 5]. Highly conducting organic substances are relatively rare. An unstable bromine/perylene complex is reported to have a resistivity of 1 ohm-cm [Ref. 7], and a metastable iodine/perylene complex is reported with a resistivity of 8 ohm-cm [Ref. 8]. For comparison, the resistivity of pure silicon is  $10^3$  ohm-cm, graphite about  $10^{-3}$  ohm-cm, and most organic compounds  $10^{10}$  to  $10^{14}$  ohm-cm [Ref. 9].

An interesting compound 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been synthesized [Ref 10], and certain of its stable anion radical derivatives exhibit very high electrical conductivity [Refs. 11, 12, and 13], with resistivities on the order of  $10^{-2}$  ohm-cm. Recently a TCNQ complex has been reported with a conductivity of  $1.47 \times 10^4$  ohm $^{-1}$  cm $^{-1}$  [Ref. 14] which compares favorably with the conductivity of copper which is  $6 \times 10^5$  ohm $^{-1}$  cm $^{-1}$ . Complexes of the anion-radical of TCNQ and various cations have been examined. An extensive study [Ref. 11] of over 100 compounds investigated the physical properties of many known donors with TCNQ as an acceptor. A search of recent literature revealed over 230 successful attempts at preparing TCNQ complexes and determining their physical properties (see Appendix A). Much theoretical work concerning the electronic behavior and the physical properties observed in TCNQ complexes has also been reported [Refs. 15-24]. Modifications of the TCNQ skeleton have also produced compounds with interesting properties [Refs. 25, 26, 27, and 28].

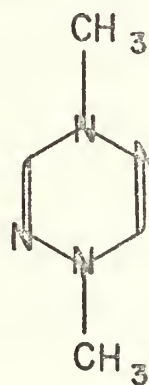
This work reports the results of a study using additional donors. Several substituted quinolines and 1,4-dimethyl-1,4-dihydro-s-tetrazine (DMDHT) were used. The DMDHT cation radical has recently been reported



and is a reasonably stable species [Ref. 29]. The cation-radical is interesting because donation of an electron to an acceptor is readily achieved without destroying the molecular skeleton of DMDHT. This work was an effort to isolate and investigate a new complex consisting of DMDHT and TCNQ. The similarity of structure between TCNQ [Refs. 30, 31, and 32] and DMDHT [Refs. 29 and 33] was another factor which would possibly allow for efficient crystal packing with subsequent higher conductivity. Several preparations and some of the observed properties of an adduct derived from TCNQ and DMDHT are presented.



TCNQ



DMDHT



## II. BACKGROUND

Quinones form stable solid complexes with aromatic amines due to interaction between the electron poor  $\pi$ -orbitals of the quinone ( $\pi$ -acid or acceptor) and the electron rich  $\pi$ -orbitals of the amine ( $\pi$ -base or donor). Some solid complexes, i.e., between aromatic diamines and relatively strong  $\pi$ -acids, show an ESR absorption. Some complexes of this type also show an exponential variation of electrical resistivity with temperature, or semiconductor behavior.

TCNQ was first reported and concurrently investigated in 1962 at E. I. DuPont DeNemours [Ref. 10]. They found that it accepts an electron to form stable anion-radical derivatives quite easily [Ref. 11]. The physical properties of these compounds were unusual, and especially noted was the occurrence of solid organic compounds having exceptionally low electrical resistivities ( $10^{-2}$  to  $10^2$  ohm-cm). TCNQ is a good  $\pi$ -acid because of the high electron affinity of the polyene system conferred by the powerful electron withdrawing action of the four cyano groups. Its planarity and high symmetry also contribute by favoring good overlap.

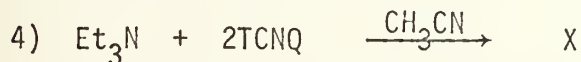
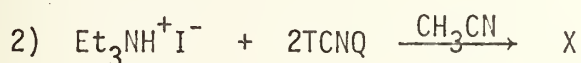
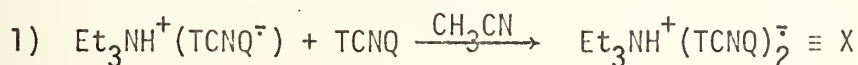
TCNQ forms three types of electrically conducting compounds: charge transfer complexes, simple salts, and complex salts. The crystalline  $\pi$ -complexes or charge transfer complexes of TCNQ with aromatic hydrocarbons, amines, and polyhydric phenols show intermediate resistivity of  $10^3$  to  $10^4$  ohm-cm and very weak ESR absorption. Stable saltlike derivatives result from the complete transfer of an electron to TCNQ.



The relationship between a  $\pi$ -complex and an anion-radical salt was shown for the case of TCNQ and diaminodurene (DAD) [Ref. 9]. In THF, TCNQ and DAD give a purple complex which is diamagnetic and can be written as  $C_{10}H_{16}N_2$  (TCNQ). It also has a high resistivity of  $10^9$  ohm-cm in powder form. However the hydriodide of DAD and TCNQ yield a blue-black anion radical complex which is paramagnetic and can be written as  $C_{10}H_{16}N_2H^+(TCNQ^{\cdot-})(TCNQ)$ . This is an example of a low resistivity salt.

Two types of TCNQ salts are common. Simple salts result from the one electron reduction of TCNQ by a metal iodide or an organic iodide in a 1:1 ratio to form  $M^+(TCNQ^{\cdot-})$ . They show intermediate to high resistivity of  $10^4$  to  $10^{12}$  ohm-cm and weak ESR absorption in the solid state. Complex salts have been found to occur only with organic donors and incorporate a neutral TCNQ molecule, with a structure written  $M^+(TCNQ)_2^{\cdot-}$ . Complete electron delocalization is believed responsible for the low resistivity of  $10^{-2}$  to  $10^3$  ohm-cm and the variable ESR of these compounds.

Four methods of synthesis exist [Ref. 11] for preparation of the complex salts. Use of the triethylammonium ion illustrates them below.



The first method requires the simple salt while the second requires the iodide salt. The iodide reduces the TCNQ to  $TCNQ^{\cdot-}$ . Method three which uses  $H_2TCNQ$  as a proton source and an electron donor was found [Ref. 11] to be most suitable for the preparation of complex salts from free amines.





In an overall sense, the physical properties of TCNQ<sup>-</sup> salts and complexes are affected by interactions among the TCNQ<sup>-</sup> moieties. Some differences due to cation structure have been observed [Refs. 34 and 35] in aliphatic homologous series. These differences are believed to be due primarily to the steric effects of the cation on the molecular packing of TCNQ in the crystal. However the effect may be due in part to electronic involvement between the cation donor and TCNQ<sup>-</sup>. Investigation of substitutions on the pyrazine ring system and analogues has shown a definite effect of cation change altering the resistivity of the complex [Ref. 36], which is not believed to be due to structural effects alone.



### III. EXPERIMENTAL

#### A. SYNTHESIS

Following the procedure of Melby [Ref 11], an unsuccessful attempt was made to directly precipitate the complex salt of quinoline and TCNQ by simple combination of the heated solutions of stoichiometric amounts of the reactants in acetonitrile. The solvents chloroform, tetrahydrofuran, methylene chloride and dioxane were also tried unsuccessfully. Melby found that the alternative procedure utilizing  $\text{H}_2\text{TCNQ}$  worked well with N-heterocyclics. Therefore it was necessary to synthesize p-phenylenedimalononitrile ( $\text{H}_2\text{TCNQ}$ ).

Since the treatment of a solution of  $\text{TCNQ}^-$  with strong mineral acids produces TCNQ and  $\text{H}_2\text{TCNQ}$  in equal molar amounts [Ref. 11], the acid decomposition of a recently prepared salt,  $\text{K}^+\text{TCNQ}^-$  was attempted. However, the resulting yellow powder did not resemble the desired product. It had an indefinite melting point of about  $215^\circ\text{C}$  and decomposed in stages. It was apparently some other decomposition product and was not examined further. A method mentioned by Acker [Ref. 10] was then tried. HI gas was passed over the surface of 10 milliliters of water in a narrow tube for 1 1/2 hours using a small inverted funnel to aid absorption of the gas into the water. The resulting acid was determined to be 39% aqueous HI by NaOH titration and density measurement. To 1.0 gm. of TCNQ suspended in 50ml of acetone, was added 3.4ml of 39% HI. This was warmed for 30 minutes over a steam bath, stirring continuously. The hot solution was filtered into a 500ml flask and 150ml of  $\text{CH}_2\text{Cl}_2$  was added. This was allowed to stand overnight, covered and at room



temperature. The product was collected by vacuum filtration and washed with  $\text{CH}_2\text{Cl}_2$  and ether and allowed to dry. The resulting micro-crystals were brownish-yellow and melted at  $238^\circ\text{-}240^\circ\text{C}$ .

Preparation of quinoline<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup> was again attempted using  $\text{H}_2\text{TCNQ}$ . Seventy-five mg of TCNQ was dissolved in 7.5ml of  $\text{CH}_3\text{CN}$  and heated to  $70^\circ\text{-}75^\circ\text{C}$ . This was added to 25.0 mg of  $\text{H}_2\text{TCNQ}$  and 32.3 mg of quinoline in 4.0ml of  $\text{CH}_3\text{CN}$  also heated to  $70^\circ\text{C}$ . The solution turned dark green immediately, indicating formation of  $\text{TCNQ}^\cdot$  [Ref. 11], and blue-black needle-like crystals began to precipitate immediately. After one hour the solution was filtered and the product washed and dried. The crystals were very light and hair-like threads. The same procedure was used with 2-methylquinoline, 4-methylquinoline, and 7-methylquinoline. All four donors produced blue-black to purplish fine crystals of 2:1 complex salts with greater than 70% yield. Quinoxaline did not yield a TCNQ complex via this method. Melby [Ref. 36] reports the synthesis of the simple and complex quinoxaline/TCNQ salts, however quaternized quinoxaline was used.

Upon completion of the preliminary preparations using quinolines, the same techniques were used with DMDHT as a donor. On mixing the hot  $\text{CH}_3\text{CN}$  solutions of DMDHT/ $\text{H}_2\text{TCNQ}$  and TCNQ the  $\text{TCNQ}^\cdot$  dark green solution formed. However, cooling produced no black crystals. Only a slightly discolored orange TCNQ was found to precipitate out. These crystals were collected and washed. ESR examination of these crystals showed a weak absorption with a g-value of about 2.002.

Preceding further investigation of this DMDHT/TCNQ product, a more thorough understanding of DMDHT was desired. Addition of DMDHT to iodine in THF produces the radical cation which has a complex ESR



spectrum of over 40 lines [Ref. 29]. A similar spectrum was obtained from TCNQ/DMDHT in  $\text{CH}_3\text{CN}$ , indicating the presence of the DMDHT radical cation. DMDHT was also added to a  $\text{AgClO}_4$  solution and a brownish precipitate formed. This complex was filtered, washed, dried and recrystallized from  $\text{CH}_3\text{CN}$ . Its ESR spectrum was a singlet with a line-width of 2.5 gauss and approximately the same g-value as the DMDHT/TCNQ singlet absorption.

Upon complete evaporation of the liquor which yielded the initial discolored orange TCNQ, a mixture of more discolored TCNQ and black microcrystals was observed. An investigation of several solvents, recrystallization and phase equilibria were unsuccessful in producing a pure  $\text{DMDHT}^+(\text{TCNQ})_2^-$  complex salt. Recrystallization left the mixture unchanged which lends additional support to the belief that the black precipitate product is a 2:1 complex salt, since the 1:1 simple salts characteristically decompose upon attempts to recrystallize them.

The characteristic  $\text{TCNQ}^-$  dark green was absent in  $\text{CH}_2\text{Cl}_2$  solutions; however,  $\text{H}_2\text{TCNQ}$  did not dissolve well either. DMDHT/TCNQ, without  $\text{H}_2\text{TCNQ}$ , in  $\text{CH}_2\text{Cl}_2$  upon standing overnight yielded greenish crystals resembling TCNQ, and upon complete evaporation, blue-black microcrystals were again observed. Rapid evaporation to dryness also yielded greenish crystals with the same general glassy appearance and morphology of TCNQ along with the second precipitated phase of blue-black microcrystals, which could be separated by scraping the sides of the vessel. Varying the stoichiometric ratio did not solve the problem. A TCNQ to DMDHT ratio of 2:1 yielded the largest amount of black crystals in the matrix, while a 1:1 ratio yielded proportionately less of the black crystalline material. A 1:2 ratio produced the most completely homogenous mixture





however even this was far from "pure". Eliminating  $\text{H}_2\text{TCNQ}$  in  $\text{CH}_3\text{CN}$  preparations produced different results also. Rather than orange TCNQ, green TCNQ precipitated. Upon evaporation to dryness, the illusive black crystals were again present, mixed with green TCNQ. The green TCNQ has a singlet ESR absorption near that for orange TCNQ and of approximately the same intensity.

A successful procedure for growing large crystals of orange and green TCNQ as well as pure TCNQ was to place a test tube containing the hot solution mixture in a dewar containing water at  $60^\circ\text{C}$  and allow it to cool to room temperature in 24 to 30 hours. The resulting crystals were approximately  $0.1\text{mm} \times 1.0\text{mm} \times 1.0\text{mm}$ . It is interesting to note that slow cooling of TCNQ and  $\text{H}_2\text{TCNQ}$  in  $\text{CH}_3\text{CN}$  produced TCNQ plus some very fine fan-like clusters of bright metallic reddish-purple crystals. These were not investigated further except to examine them by ESR. They possessed a very weak absorption with an unusual lineshape (Figure 1) with a g-value of approximately 2.002. The lineshape resembles a narrow absorption superimposed upon a broad absorption.

## B. INSTRUMENTATION

ESR measurements were conducted with a Varian 4502-13 X-band spectrometer with Fieldial V-FR-2503 magnetic field and associated 9-inch electromagnet using 100kc field modulation. The cavity was a standard reflection type. A Varian variable temperature accessory V-4557 with 4540 controller was used to vary the temperature. The sample was supported in a dewar extending through the microwave cavity. Temperature variation was achieved by passing heated or cooled nitrogen about the sample. Accurate temperature measurements were made by use of a copper-constantan thermocouple placed in the dewar approximately one-half inch



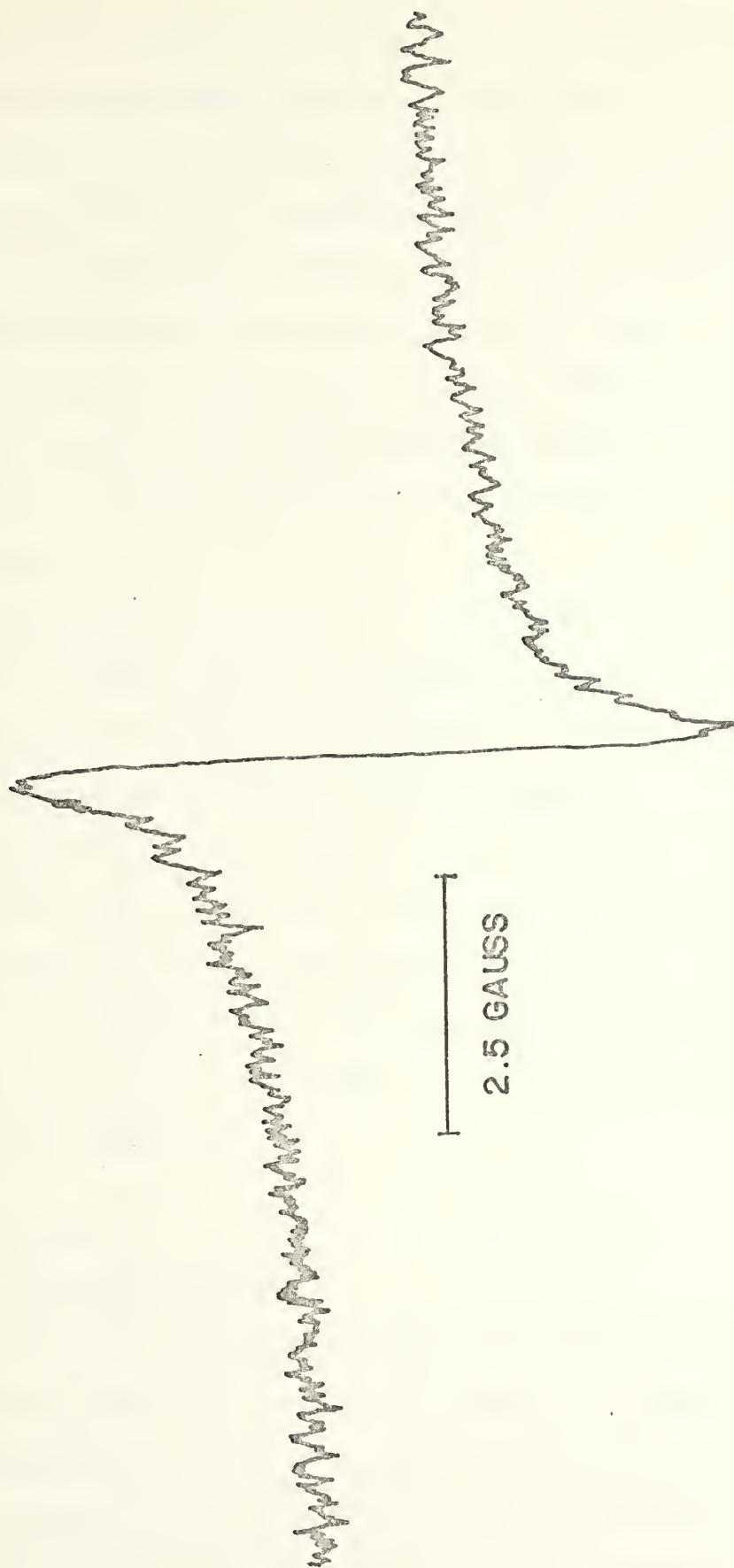


Figure 1. ESR first derivative absorption spectrum of reddish-purple crystals resulting from TCNQ/H<sub>2</sub>TCNQ mixture.



above the sample, just out of the cavity. The Hewlett-Packard 419A DC Null Voltmeter and Acromag copper-constantan Type T, 0°C reference were checked and calibrated using ice water and liquid nitrogen.

Calibration of the ESR incremental magnetic field control was done using  $K_2(SO_3)_2NO$  in  $Na_2CO_3$  solution. Magnetic field splittings for this triplet were determined previously in this laboratory to be 13.064 and 13.115 gauss by comparison with a locked-in NMR magnetometer and frequency counter. Using these values a correction of 1.3% was found to be necessary to convert the measured field differences to true field differences.

Freshly grown single crystals of  $CuSO_4 \cdot 5H_2O$  were used as spin density standards. Weighed crystals were sprayed with varnish and sealed in a capillary tube or covered with Duco cement to prevent dehydration. A  $CuSO_4 \cdot 5H_2O$  standard was used to check the linearity of the spectrometer signal level control. The absorption line height was a linear function of the signal level control over the order of magnitude difference in scales which was checked. Using the reported g-value of 2.00360 [Ref. 37] for polycrystalline 2,2-diphenylpicryl hydrazine (DPPH), and two transitions due to  $Mn^{++}$  in  $MgO + 0.2\%MnCl_2$ , the g-values of the samples were determined.

## C. PROCEDURES

### 1. Quinoline Complexes

Of the four quinoline complexes only quinoline<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup> forms individually discernable thread-like crystals. The other three result in complexes which consist of extremely small microcrystals. All four samples showed extremely intense anisotropic ESR absorptions with a linewidth of approximately 2.7 gauss. A typical spectrum is shown in



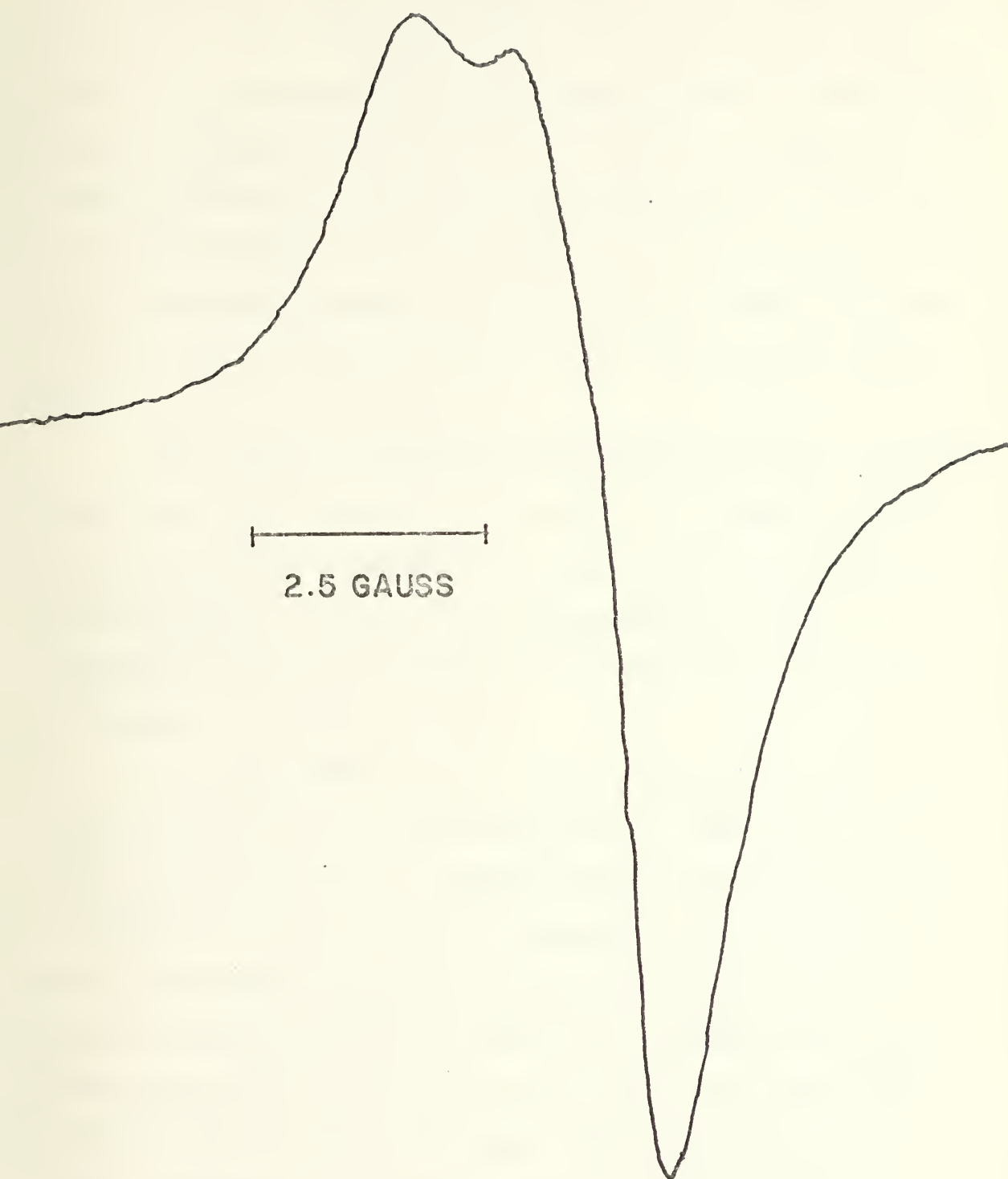


Figure 2. Typical anisotropic ESR absorption exhibited by the four quinoline/TCNQ (2:1) complexes.





Figure 2. The ESR absorption was so intense that in order to resolve the anisotropy and determine g-values sample size was limited to less than 0.1mg. However these samples were still polycrystalline. The parallel ( $g_{\parallel}$ ) and perpendicular ( $g_{\perp}$ ) g-components were determined by the method described by Kneubühl [Ref. 38]. For an axially symmetric g-tensor the value for  $g_{\parallel}$  and  $g_{\perp}$  can be determined from the first derivative of the absorption curve. The value of  $g_{\parallel}$  is taken from the value of the field at the shoulder, and the value of  $g_{\perp}$  is taken at the point of maximum slope. Anisotropic spectra can be dealt with in a similar manner.

Bulk magnetic susceptibility measurements were made by the Faraday method using a Cahn Electrobalance, model DTL, in conjunction with a 5700 gauss permanent magnet which was rolled in and out of position to make measurements. Mercury(II)tetrathiocyanatocobaltate(II),  $\text{Hg}[\text{Co}(\text{CNS})_4]$ , was used as a standard with a susceptibility of  $16.44 \times 10^{-6}$  emu/gm.

Pressed pellets of the four quinoline complexes were made using a 0.716 cm diameter die and 6000 pounds pressure. Samples were on the order of 20mg and resulted in pellets ranging from 0.035 cm to 0.050 cm in thickness. A simple two contact procedure was used to measure the pellet resistances. Silver paint was used to cover the surfaces of the pellet and connect short copper leads. Using a Hewlett-Packard 6216A Power Supply with 0 to 30 volt range and a Weston 1240 digital ammeter in series with the sample to be tested, the voltage drop across the sample was measured using a Hewlett-Packard 419A DC Null Voltmeter with an impedance of  $10^5$  ohms. (Figure 3.) The internal resistance of the system consisting of voltmeter leads, copper wire sample leads, and



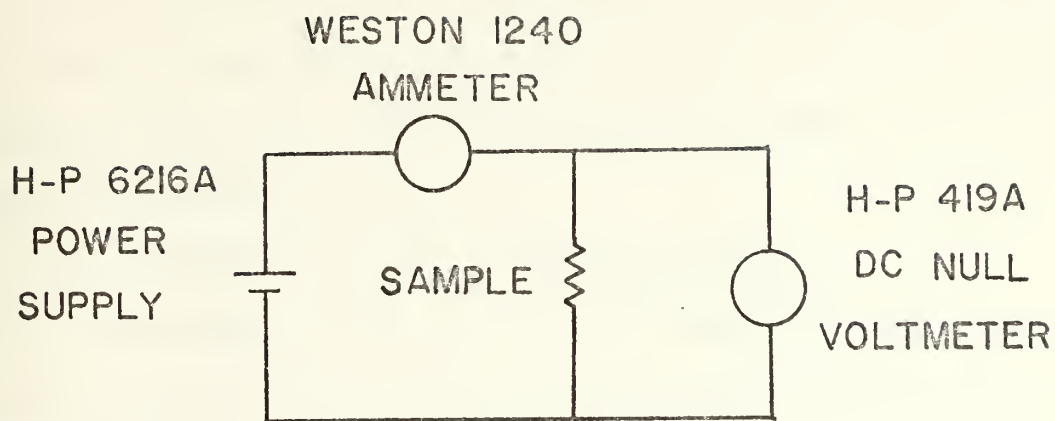


Figure 3. Diagram of circuit used for determination of the resistivity of pellet samples.

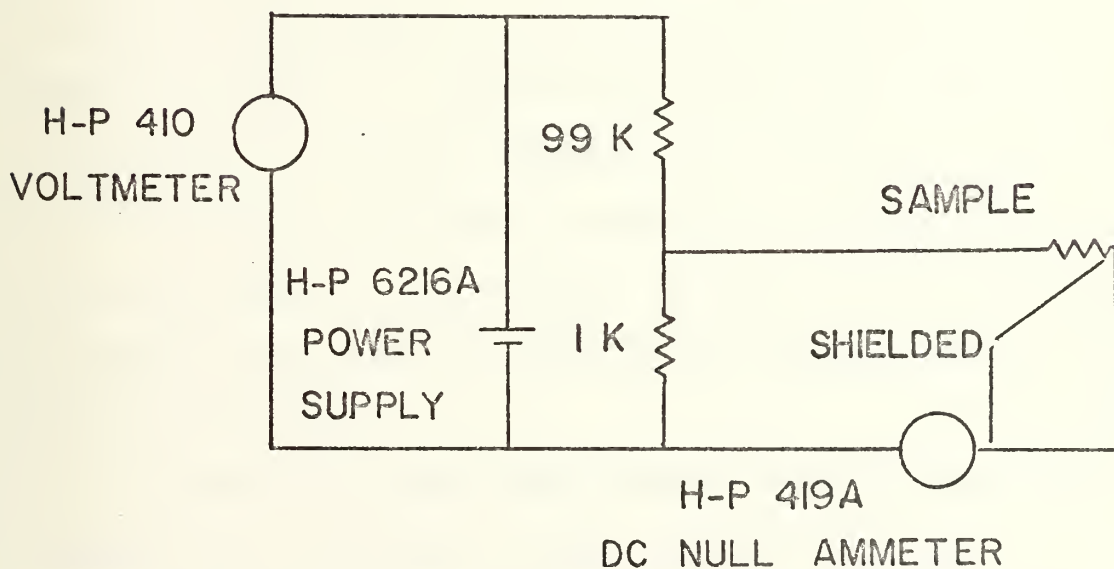


Figure 4. Diagram of bridge circuit used for the determination of single crystal resistivities.



silver contact paint was determined to be 0.018 ohm by using an intentionally shorted sample. This resistance was assumed to be negligible. It should be noted that in these high conductivity materials, contact resistance can be appreciable [Ref. 39] and four electrode measurements should be made where possible.

## 2. 1,4-Dimethyl-1,4-dihydro-s-tetrazine Complex

Slow cooling of the mixture of TCNQ,  $H_2TCNQ$  and DMDHT produced single crystals of orange TCNQ which possessed a weak ESR absorption whereas pure TCNQ grown in the same manner exhibited no ESR. It is also worth noting that the TCNQ recovered from the early unsuccessful attempts to produce the quinoline TCNQ salts and quinoxaline salt did not possess any ESR. The DMDHT doped TCNQ crystals were on the order of 0.08 cm x 0.08 cm x 0.01 cm so individual crystal measurements were possible.

A doped TCNQ crystal and a  $CuSO_4 \cdot 5H_2O$  standard coated in Duco cement were affixed with stopcock grease to the flattened side of a specially prepared quartz rod. The rod (4mm diameter with 1.5mm removed from one side) was mounted on a holder which allowed positioning the crystal in the dewar. The temperature was varied from  $-171^\circ C$  to  $60^\circ C$ , at which point the  $CuSO_4 \cdot 5H_2O$  standard began to dehydrate. The intensity of the absorption of doped TCNQ relative to  $CuSO_4 \cdot 5H_2O$  was calculated by the method of first moments. The ESR first derivative absorption spectra were initially recorded on graph paper to facilitate numerical integration.

A single 0.5mg doped TCNQ crystal was visually aligned on an adjustable Delrin goniometer which was then mounted in the cavity in such a manner as to allow rotation of the crystal about both axes perpendicular to the direction of the magnetic field. In this way data for determination of the g-tensors could be collected. Eight measurements of different



crystal orientations yielding an essentially isotropic g-value of 2.00278 ( $\pm 0.00003$ ) relative to DPPH (2.00360).

Since the doped TCNQ possessed an isotropic absorption, the temperature study was repeated using a bulk sample of several milligrams. This allowed lower gain spectrometer settings and consequently the data had less noise and was more easily interpretable. The bulk sample temperature study was also carried out at a lower power level since preliminary measurements showed appreciable power saturation at low temperatures. Analysis of this data resulted in a significantly altered relationship between the absorption intensity and temperature for doped TCNQ (Figure 5).

Resistivity measurements of single crystals of DMDHT doped TCNQ were accomplished by a technique similar to that used for the quinoline pellets. Since the samples were two dimensional, flat crystals, measurements were made perpendicular to the flat face ( $\rho_{\perp}$ ) of the crystal as well as along the face ( $\rho_{\parallel}$ ) of the crystal. The same crystal morphology was observed in pure TCNQ (Figure 6). Short, narrow gauge, copper wires were attached to the desired crystal faces by means of silver paint. A stereoscopic microscope was used in order to facilitate handling these small samples. The sample with both leads attached was then dipped in epoxy to strengthen it against mechanical damage. Finally the leads were extended with insulated copper wire and the sample device was taped to a quartz rod (4mm diameter) for insertion into the variable temperature ESR dewar, as shown in Figure 7. The size of the samples precluded the use of the four probe method.

The experimental bridge circuit used to measure the resistance of each single crystal sample is shown in Figure 4. The VTVM measured





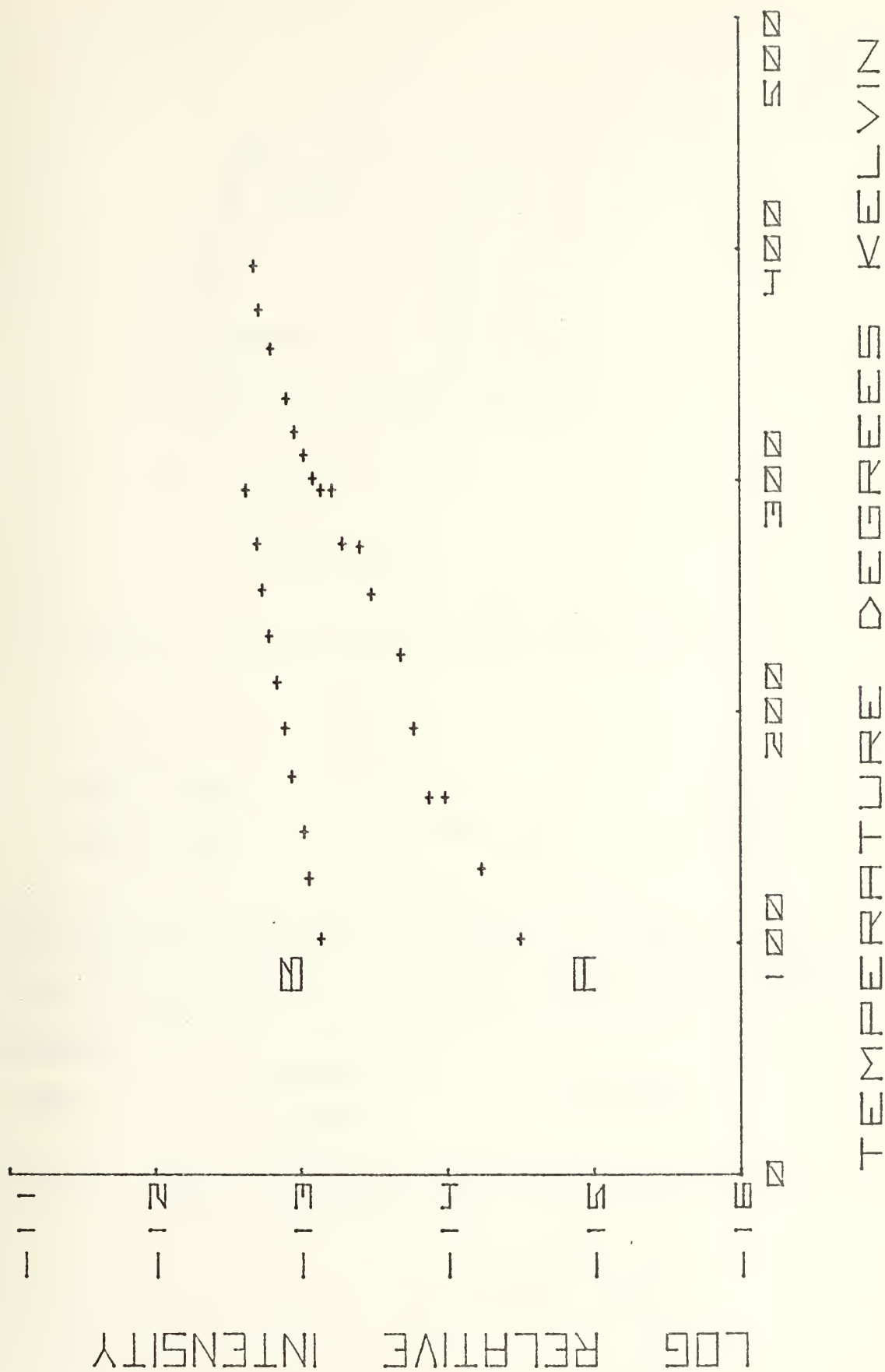


Figure 5. Absorption intensity versus temperature showing effect of power saturation in a single crystal (a), and a bulk sample at a lower power level (b).



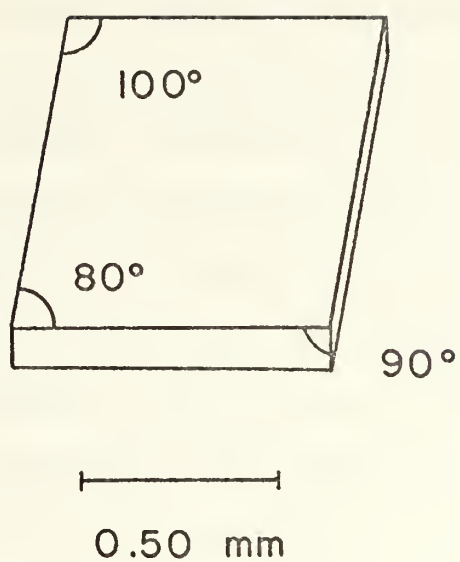


Figure 6. Crystal morphology of DMDHT doped TCNQ compound.

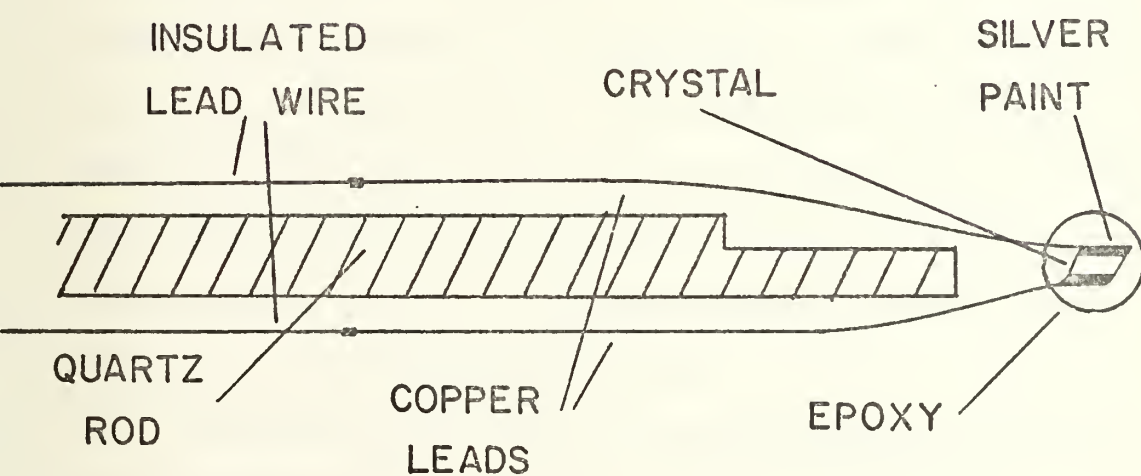


Figure 7. Device for measuring single crystal resistivities while in variable temperature dewar.



the source voltage which was reduced by a factor of 100 by a voltage divider. The 99K ohm and 1K ohm voltage divider decade resistance boxes were checked with an impedance bridge and were found to be accurate to within 1%. The current flowing through the sample was measured using a low impedance ammeter. From the scale calibrations of the H-P 419A DC Null Voltmeter/Ammeter itself the impedance was determined to be  $10^5$  ohms. This was checked by using two high value resistors of precisely known resistance and calculating the resistance of the ammeter, by voltage and current measurements. Since the sample resistance measured were on the order of  $10^8$  and greater, the impedance of the ammeter could be neglected.

A control sample consisting of two copper leads in only the epoxy, separated by the approximate crystal width had a resistance greater than  $10^{12}$  ohms. It was found to be necessary to shield the lead from the sample to the ammeter in order to reduce the effects of ambient static charges. Insertion in the dewar eliminated this problem almost entirely. The resistance of the sample was determined by measuring the current flow at a set voltage. From the measured resistance and the dimensions of the sample the resistivity was calculated. A 2.00mm grid with 0.01mm divisions was used under the stereo microscope to accurately determine the dimensions of each sample before the second lead was attached and they were dipped in epoxy.

Resistivity as a function of temperature was measured using the variable temperature dewar. The minimum current measureable was  $1 \times 10^{-13}$  amps and the maximum voltage was 0.1 volt so this limited the temperature at which measurements could be made. Data was not taken above 70°C in order to avoid any complications arising from possible decomposition of the sample.



No effective method of producing pure black crystals of DMDHT/TCNQ could be devised, since usually TCNQ was also a major product. Resistivity measurements of a pellet of the resulting impure DMDHT/TCNQ complex with TCNQ were made. Partial evaporation of the  $\text{CH}_2\text{Cl}_2$  mixture deposited the lighter, black, less soluble crystals of DMDHT/TCNQ on the walls of the beaker, while complete evaporation of the solution resulted in a mixture of TCNQ and complex on the bottom. The relatively pure DMDHT/TCNQ was collected from the sides. ESR measurements were made on this material and the anisotropic g-values were determined. Bulk magnetic susceptibility and pellet resistivity measurements were also made using this sample. The same apparatus and techniques were used as with the quinolines.

Further ESR investigation of samples failed to exhibit the  $\Delta M = \pm 2$  forbidden transition, characteristic of the triplet state. Bulk samples of both orange and green doped TCNQ were examined.

During the single crystal temperature studies it was noticed that certain irreversible changes occurred in the ESR absorption at high temperatures. A freshly grown crystal was examined from 23°C to 250°C affixed to the flattened side of a quartz rod with stopcock grease. The spectrum was recorded at each temperature. The temperature was then raised about 20°C and the spectrum was again recorded. After each new temperature the sample was returned to room temperature and the spectrum checked to see if any irreversible change had occurred due to the time at higher temperatures. The sample was removed and examined under the stereo microscope after each temperature cycle. The sample was reinserted in the dewar and the procedure repeated for the next temperature, until the maximum limit of the instrument was reached. A bulk sample of doped





TCNQ was similarly studied, as well as a bulk sample of pure TCNQ. Since irreversible changes were noticed not only with temperature but also with time, a kinetic study was run. A bulk sample of doped TCNQ was heated from room temperature to 185°C and the ESR spectrum was continuously monitored for 100 minutes. The "decay" of the ESR absorption with time was observed.



#### IV. RESULTS AND DISCUSSION

The ESR absorption of each of the quinoline complexes was found to be anisotropic in varying degrees. The  $g_{||}$  and  $g_{\perp}$  values of the four quinoline complexes are presented in Table I. Several different samples of DMDHT/TCNQ were examined. They were different primarily in the method of preparation. These polycrystalline samples had an average g-value of 2.00314 but ranged from 2.00288 to 2.00329. Table I also includes the values of  $g_{||}$  and  $g_{\perp}$  determined for DMDHT/TCNQ from an average sample.

The bulk magnetic susceptibilities of the quinoline complexes are listed in Table I along with the previously reported values for quinoline<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup>. Using the relatively pure DMDHT/TCNQ collected from the side of the beaker, a magnetic susceptibility was determined for the 1,4-dimethyl-1,4-dihydro-s-tetrazine TCNQ complex (Table I). It can be seen that the susceptibility of DMDHT/TCNQ is twice that of the most susceptible quinoline, even in an impure state.

The calculated resistivities of the quinoline complexes are tabulated in Table II, and agree reasonably well with values for similar reported substances. Melby [Ref. 11] found that compactions usually had resistivities one or two orders of magnitude higher than single crystals, due primarily to interparticle boundaries. The impedance of these pellet samples was the same when the polarity of the leads was reversed. The resistivity of a pellet of the DMDHT/TCNQ complex with TCNQ as a gross impurity was also determined (Table II). The high  $\rho$  value is due at least in part to the large amount of TCNQ present in the pellet. A pellet was made from the same "pure" DMDHT/TCNQ used to determine a



TABLE I  
Magnetic Susceptibility and g-values  
of  
Donor<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup> Complex Salts

Donor	g ±0.00002	g ±0.00004	$\chi \pm 1 \times 10^{-7}$ (emu/gm)
Quinoline	2.00255 <sup>a</sup>	2.00341 <sup>b</sup>	$3 \times 10^{-7}$ <sup>c d</sup>
2-Methylquinoline	2.00273	2.00322	$5 \times 10^{-7}$
4-Methylquinoline	2.00255	2.00321	$-3 \times 10^{-7}$
7-Methylquinoline	2.00259	2.00332	$6 \times 10^{-7}$
DMDHT A <sup>e</sup>	2.00288	2.00411	
B <sup>f</sup>	2.00282	2.00405	
isotropic g-values ±0.00002			
C <sup>g</sup>	2.00325		
D <sup>h</sup>	2.00312		
E <sup>i</sup>	2.00306		
F <sup>j</sup>	2.00329		
G <sup>k</sup>	2.00328		
H <sup>l</sup>	2.00311		$11 \times 10^{-7}$

(a) Previously reported value 2.00320 [Ref. 46].

(b) Previously reported value 2.00240 [Ref. 46].

(c) Previously reported value  $2 \times 10^{-7}$  emu/gm [Ref. 47].

(d) Previously reported value  $4 \times 10^{-7}$  emu/gm [Ref. 49].

(e) through (l) Methods of Preparation

(e) 2:1 stoichiometric mixture of reactants TCNQ:DMDHT, using H<sub>2</sub>TCNQ, in acetonitrile, evaporation to dryness overnight.

(f) 1:1 stoichiometric mixture, without H<sub>2</sub>TNCQ, in acetonitrile, slowly cooled in dewar of water at 60°C.

(g) 2:1 mixture, without H<sub>2</sub>TNCQ, in acetonitrile, slowly cooled.

(h) 2:1 mixture, with H<sub>2</sub>TCNQ, in acetonitrile, slowly cooled.

(i) 1:2 mixture, without H<sub>2</sub>TCNQ, in acetonitrile, slowly cooled.

(j) 1:2 mixture, without H<sub>2</sub>TCNQ, in dichloromethane, slowly cooled.

(k) 1:1 mixture, with H<sub>2</sub>TCNQ, in dichloromethane, evaporation overnight.

(l) 2:1 mixture, without H<sub>2</sub>TCNQ, in acetonitrile, evaporation overnight.



TABLE II

Pellet Resistivity  
of  
Donor<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup> Complex Salts

Donor	Resistivity (ohm-cm)	Previous Values (ohm-cm)
Quinoline	3.8	0.5 <sup>a</sup> , 0.25 <sup>b</sup>
2-Methylquinoline	3.7	0.6 <sup>c</sup>
4-Methylquinoline	15.2	
7-Methylquinoline	24.3	
DMDHT D <sup>d</sup>	$2.8 \times 10^4$	
H <sup>e</sup>	$2.6 \times 10^4$	

(a) [Ref. 48], (b) [Ref. 59], (c) [Ref. 48], (d) Sample with large quantity of TCNQ impurity, (e) Sample scraped from side of beaker, "relatively pure" sample.

TABLE III

Activation Energy  
of  
Single Crystals

Sample	Activation Energy (eV)	Previous Values (eV)
Doped TCNQ $\rho_{\perp}$	0.55	0.40-0.65 <sup>a</sup>
Doped TCNQ $\rho_{\parallel}$	0.43	
TCNQ $\rho_{\perp}$	0.66	
TCNQ $\rho_{\parallel}$	0.56	

(a) [Ref. 43]





magnetic susceptibility and the resistivity was found to be relatively the same. TCNQ could be seen in this sample pellet too.

At 23°C the ESR absorption intensity of a weighed sample of doped TCNQ was compared to the absorption intensity of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  standard. The absolute spin density of orange doped TCNQ was found to be  $1.3 \times 10^{19}$  unpaired electrons per mole of TCNQ, and for green doped TCNQ the spin density was  $1.4 \times 10^{19}$  unpaired electrons per mole of TCNQ. The g-values are 2.00247 and 2.00276 respectively.

The intensity of an ESR absorption is proportional to the area under the absorption curve.

$$I \propto A = \int f \, dx$$

The actual recorded ESR signal is  $f'$ , the derivative of the absorption.

The first moment of the derivative curve is

$$\int_{-\infty}^{\infty} x \, f' \, dx$$

and integration by parts yields

$$\int_{-\infty}^{\infty} x \, f' \, dx = x \, f \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f \, dx$$

For a Lorentzian line

$$f = 1/(1+a^2 x^2)$$

so  $f$  approaches zero as  $x$  approaches infinity and the product of  $x \, f$  evaluated at infinity is zero. The result is that

$$\int_{-\infty}^{\infty} x \, f' \, dx = - \int_{-\infty}^{\infty} f \, dx = M$$

where  $M$  is the intensity by first moments.

Using the expression

$$f = 1/(1+a^2 x^2)$$

for a Lorentzian line and setting the second derivative equal to zero, the halfwidth of the absorption can be found,

$$x_{1/2} = 1/(a \sqrt{3})$$



The intensity constant, I, at this point can be found from the expression

$$I = (f'(x_{1/2})8\sqrt{3})/(9a)$$

The two parameters a and I can be determined directly from the sample spectrum, and the corresponding true Lorentzian line shapes could then be drawn using a Hewlett-Packard programable calculator/plotter. The line shape of both  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and doped TCNQ were Lorentzian.

Integration was accomplished by a modification of Simpson's Rule so that rather than integrating

$$\int_{x_0}^{x_2} f \, dx$$

the function

$$\int_{x_0}^{x_2} x^2 f' \, dx$$

was integrated. Again a programable Hewlett-Packard calculator was used for the calculations. The abscissa was automatically incremented, thus the ordinate values from the graph were the only data inputs needed.

To correct for a finite integration interval, the weakest ESR spectrum was used to determine the limit at which accurate measurement of displacement was still possible. This interval was converted to halfwidths. For a Lorentzian line shape,

$$\int_{-\infty}^{\infty} dx/(1+a^2x^2) = 1/a(\tan^{-1} ax) \Big|_{-\infty}^{\infty} = \pi/a$$

For an arbitrary number of halfwidths, w, the expression

$$\int_{-w/\sqrt{3}a}^{w/\sqrt{3}a} dx/(1+a^2x^2) = (1/a) \tan^{-1} ax \Big|_{-w/\sqrt{3}a}^{w/\sqrt{3}a} = (2/a) \tan^{-1} w/\sqrt{3}$$

was used. Therefore,

$$2 \tan^{-1} w/\sqrt{3} / \pi \times 100$$

gives the percentage of the true area calculated. All the measured first moment intensities, M, were converted to "true" Lorentzian intensities, M\*, in this way. The integration intervals used ranged from eight to fourteen halfwidths. Typically 40 data points were used for the first moment calculations.



This analysis uses the fact that the product  $x f$  evaluated at infinity is zero, however when finite integration limits are used this is not true. The difference may be significant. Integrating over the interval  $-d$  to  $d$  introduces the additional factor

$$-2ad/(1+a^2d^2)$$

or in terms of halfwidths,

$$-(2w/\sqrt{3})/(1+w^2/3)$$

The correct formula for adjusting the measured first moment integration result,  $F(w)$ , to the corresponding true Lorentzian first moment area is

$$\frac{\pi F(w)}{2[(\tan^{-1} w/\sqrt{3}) - (w/\sqrt{3})/(1+w^2/3)]} = M^{**}$$

where  $M^{**}$  is the actual Lorentzian area. The negative term was not included in the corrections used in this work. It is estimated that a maximum error of 5% was possible in this approximation, and that the conclusions herein would not be affected by the difference.

By comparing the absorption intensities, calculated by first moments, of the doped TCNQ crystal to the known  $1/T$  behavior of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  standard, information concerning the effect of temperature variation from  $-171^\circ\text{C}$  to  $60^\circ\text{C}$  on doped TCNQ could be gained. Analysis of a single crystal of doped TCNQ at a high power level showed the intensity of the ESR absorption to be increasing exponentially with temperature, as shown in Figure 5(a). It was thought that this might be the result of looking at only part of the intensity function of an excited state triplet [Ref. 40].

In the excited state triplet case

$$I \propto 1/T(3e^{\Delta E/kT})$$

where  $\Delta E$  is the activation energy of the triplet. The parameters which describe a given excited triplet state may be determined in the following



manner: Using

$$f = I/T(3+e^{\Delta E/kT})$$

as the expression for the intensity of an excited state triplet absorption [Ref. 41].

$$\log f = \log I + \log 1/T(3+e^{\Delta E/kT})$$

where

$$\log 1/T(3+e^{\Delta E/kT})$$

describes the shape of the curve as a function of one parameter,  $\Delta E/k$ , and  $\log I$  only moves the curve vertically. Thus, plots of  $\log f$  versus  $T$  can be constructed with only  $\Delta E/k$  as a parameter. This was done for the expression describing an excited state triplet and Figure 8 shows  $\log f$  versus  $T$  for various values of  $\Delta E/k$ . Figure 9 shows the experimental results of (a) the single crystal of doped TCNQ with the effects of power saturation and (b) the bulk sample of doped TCNQ at a lower power level. Figure 9 is plotted on the same scale as Figure 8 for comparison with an excited state triplet. From this it can be estimated that the unpaired electrons in doped TCNQ behave as an excited state triplet with an energy of activation of approximately 0.02 eV. Temperatures below 100°K were not attainable with the experimental apparatus available, therefore excited state triplet behavior could not be conclusively verified.

The method of first moments and correcting the intensities of the Lorentzian absorption for finite integration limits was applied to the intensity of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  standard at temperatures from -171°C to room temperature. Since the unpaired electrons in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are essentially non-interacting,

$$M^* = C/T \text{ or } M^* T = C$$

where  $C$  is a constant. This is true only if the microwave cavity is ideal. Due to the non-ideality of the cavity,  $M^* T$  is not a constant.





# TEMPERATURE DEPENDENCE OF EXCITED TRIPLET STATES

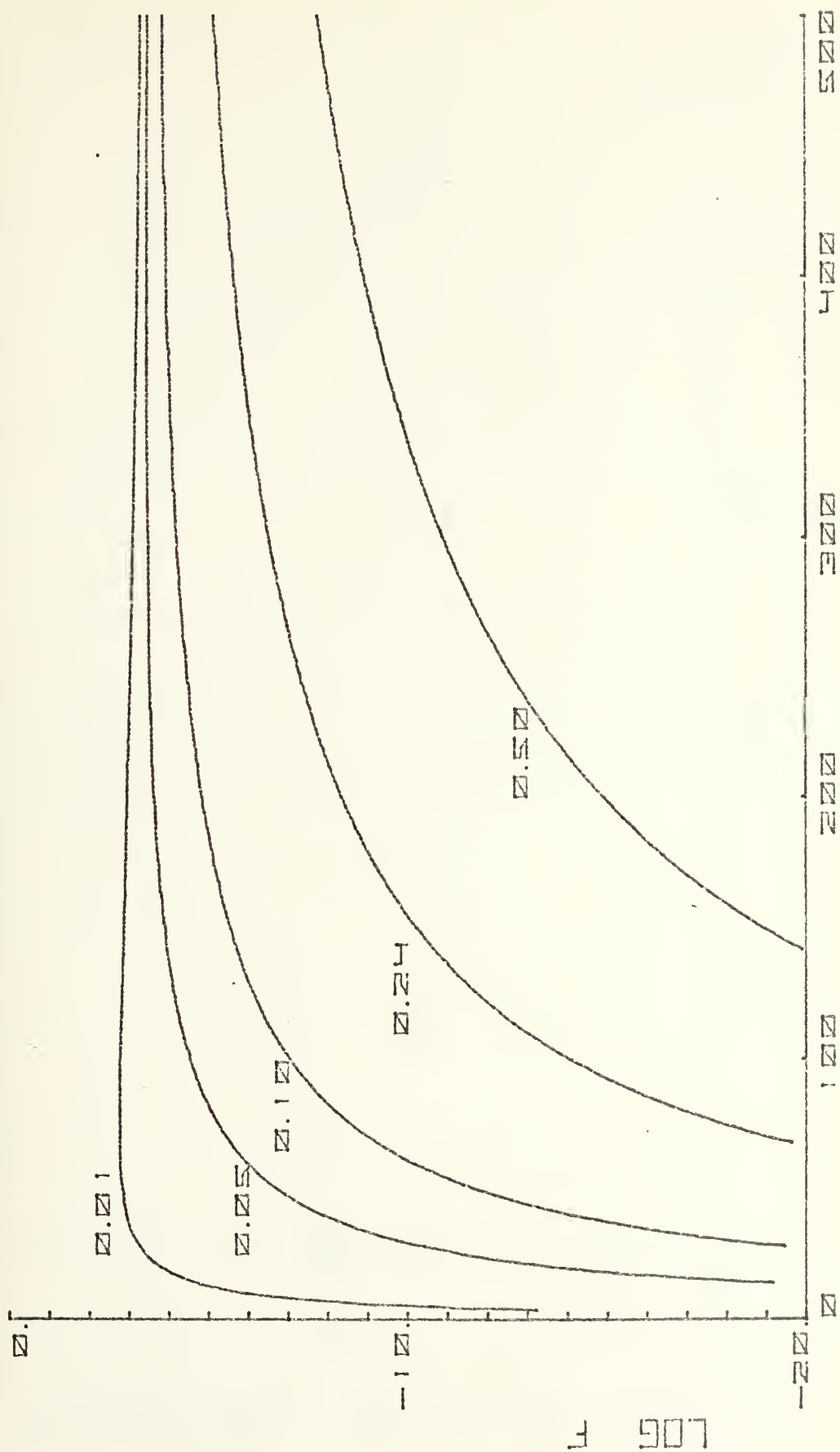


Figure 8. Plot of intensity of excited triplet states as a function of  $\Delta E/k$ .



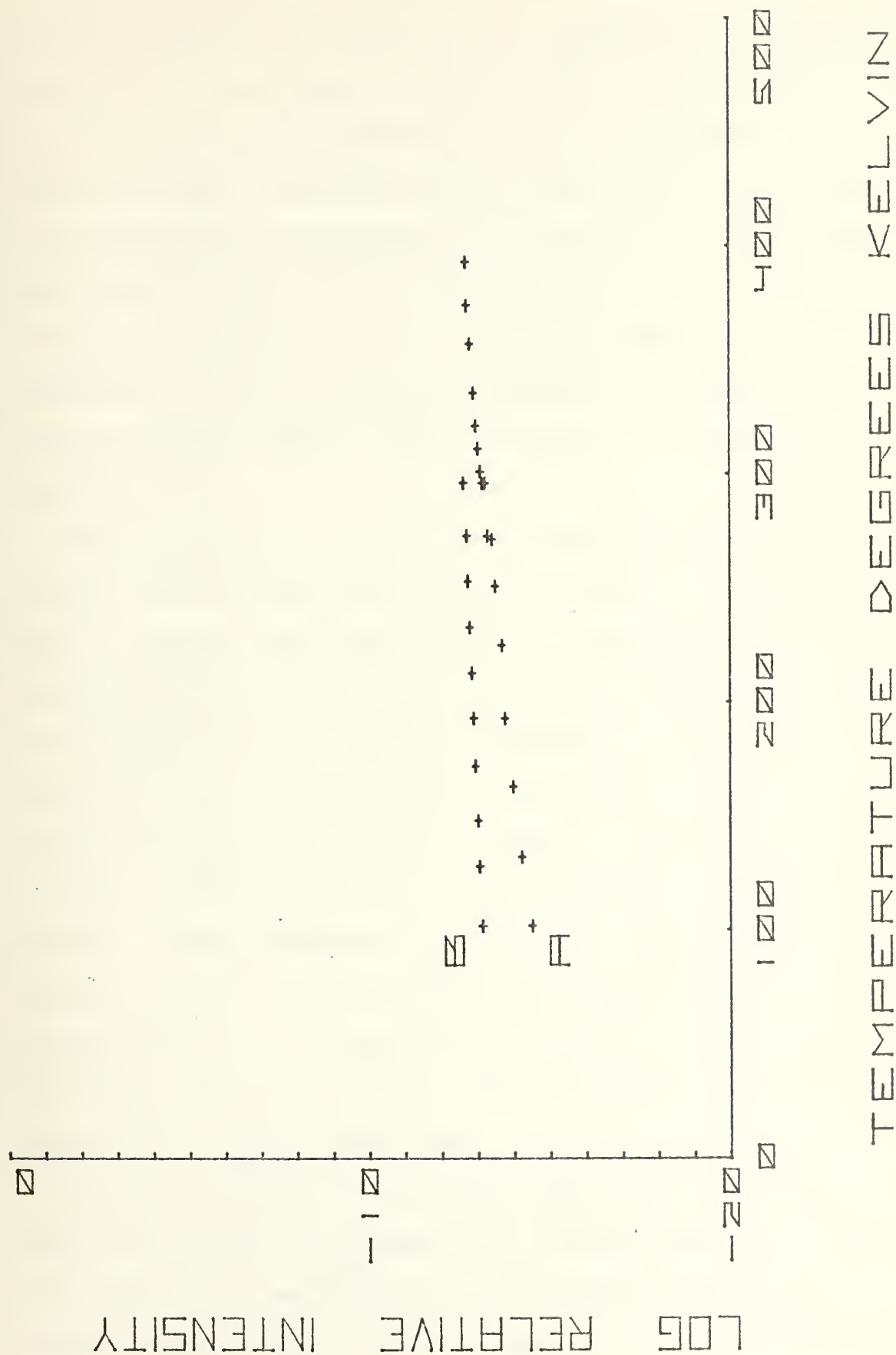


Figure 9. Relative absorption intensity versus temperature for (a) single crystal showing power saturation, and (b) bulk sample at lower power level, plotted on same scale as Figure 8 for comparison.



Figure 10 shows  $M^* T$  as a function of  $T$ . To correct for this non-ideality, a factor  $F(T)$  was determined at each temperature so that  $M^* T$  was a constant. The plot was also normalized to unity at room temperature to simplify this task. Using the correction factor  $F(T)$ , the intensities of the bulk doped TCNQ absorptions were corrected to true first moment intensities,  $M^*(\text{TCNQ})$ . Figure 11 shows the corrected  $M^*(\text{TCNQ})$  as a function of temperature. As can be seen,  $M^*$  is almost a constant at all temperatures. A metal or species with electrons in a conduction band have an absorption intensity which is constant at all temperatures [Ref. 42].

The resistivities of single crystals of doped TCNQ provide interesting data when viewed in conjunction with the ESR results. Multiple measurements of a number of doped TCNQ crystals, at room temperature, enabled determination of an average value for each type of sample. Pure TCNQ has a value for  $\rho_{\perp}$  (the resistivity perpendicular to the flat face of the crystal) of  $1.2 \times 10^9$  ohm-cm while  $\rho_{\parallel}$  (the resistivity parallel to the flat face of the crystal) is  $4.0 \times 10^8$  ohm-cm. The orange doped TCNQ has a  $\rho_{\perp}$  of  $1.3 \times 10^8$  ohm-cm and a  $\rho_{\parallel}$  of  $2.2 \times 10^7$  ohm-cm. The standard deviation of these measurements was  $5.0 \times 10^6$ . The green doped TCNQ crystals which are believed to have a higher dopant concentration had resistivities of  $4.0 \times 10^7$  ohm-cm for  $\rho_{\perp}$  and  $1.9 \times 10^7$  ohm-cm for  $\rho_{\parallel}$ . Hiroma [Ref. 43] found a value for  $\rho$  on the order of  $5 \times 10^{11}$  ohm-cm for vacuum sublimed single crystal TCNQ.

The variable temperature resistivity measurements showed that the conductance of doped TCNQ increases with increasing temperature. This is characteristic of a semiconductor and opposite that expected for a metallic substance. From the results shown in Figure 12, an energy of



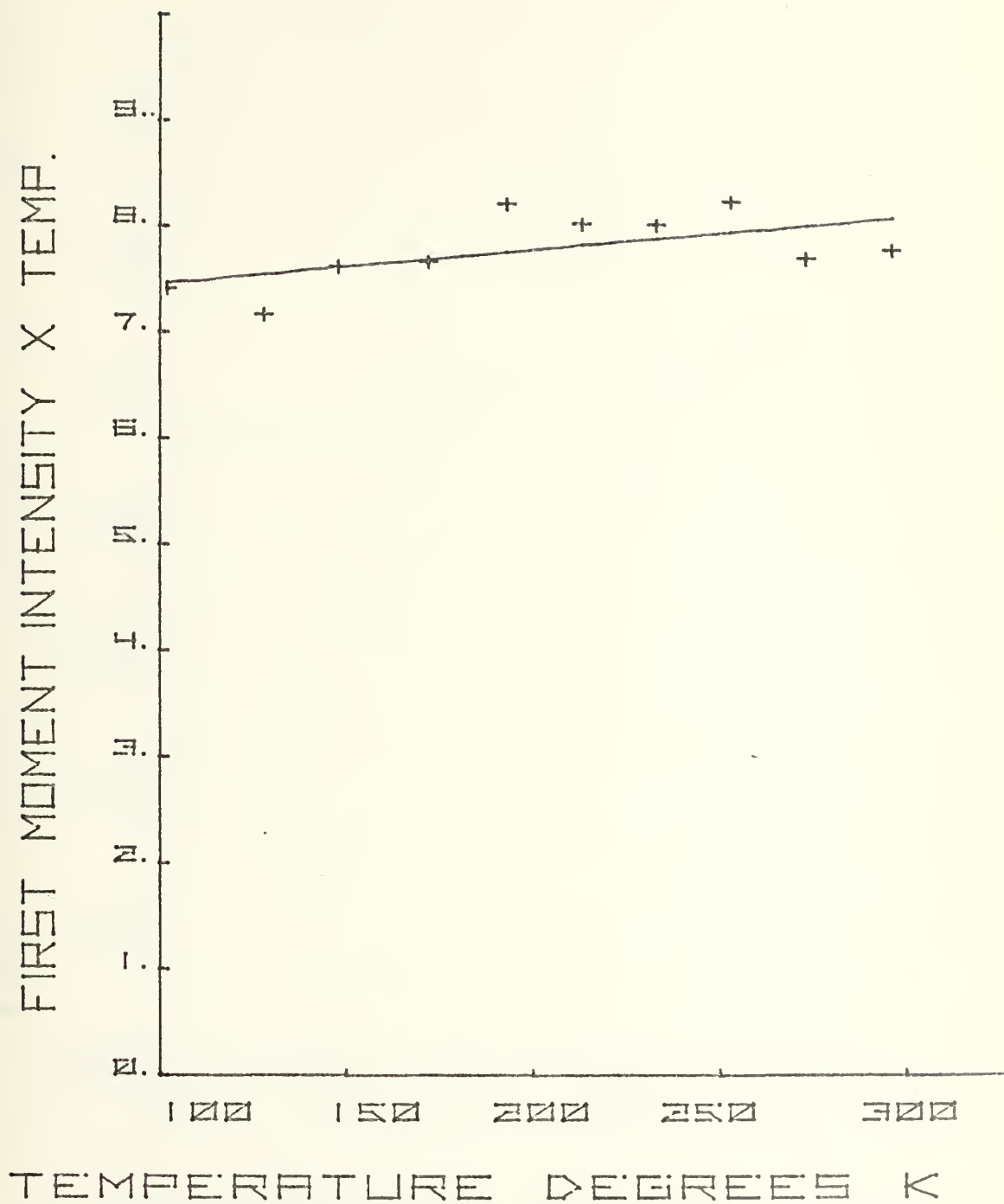


Figure 10. Plot of  $M^*(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})T$  as a function of  $T$ .





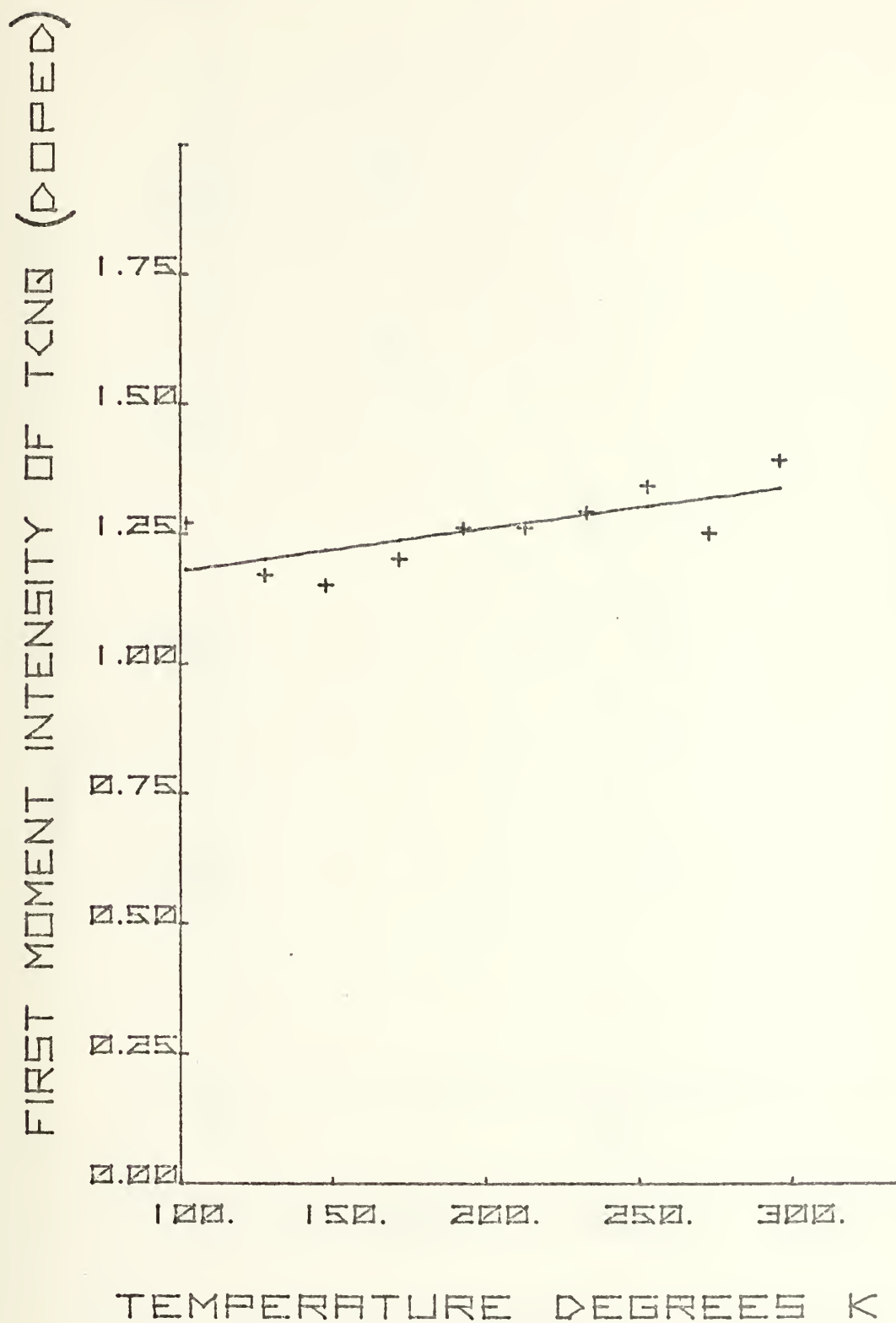


Figure 11.  $M^*(TCNQ)$  as a function of temperature, corrected for non-ideality of cavity.



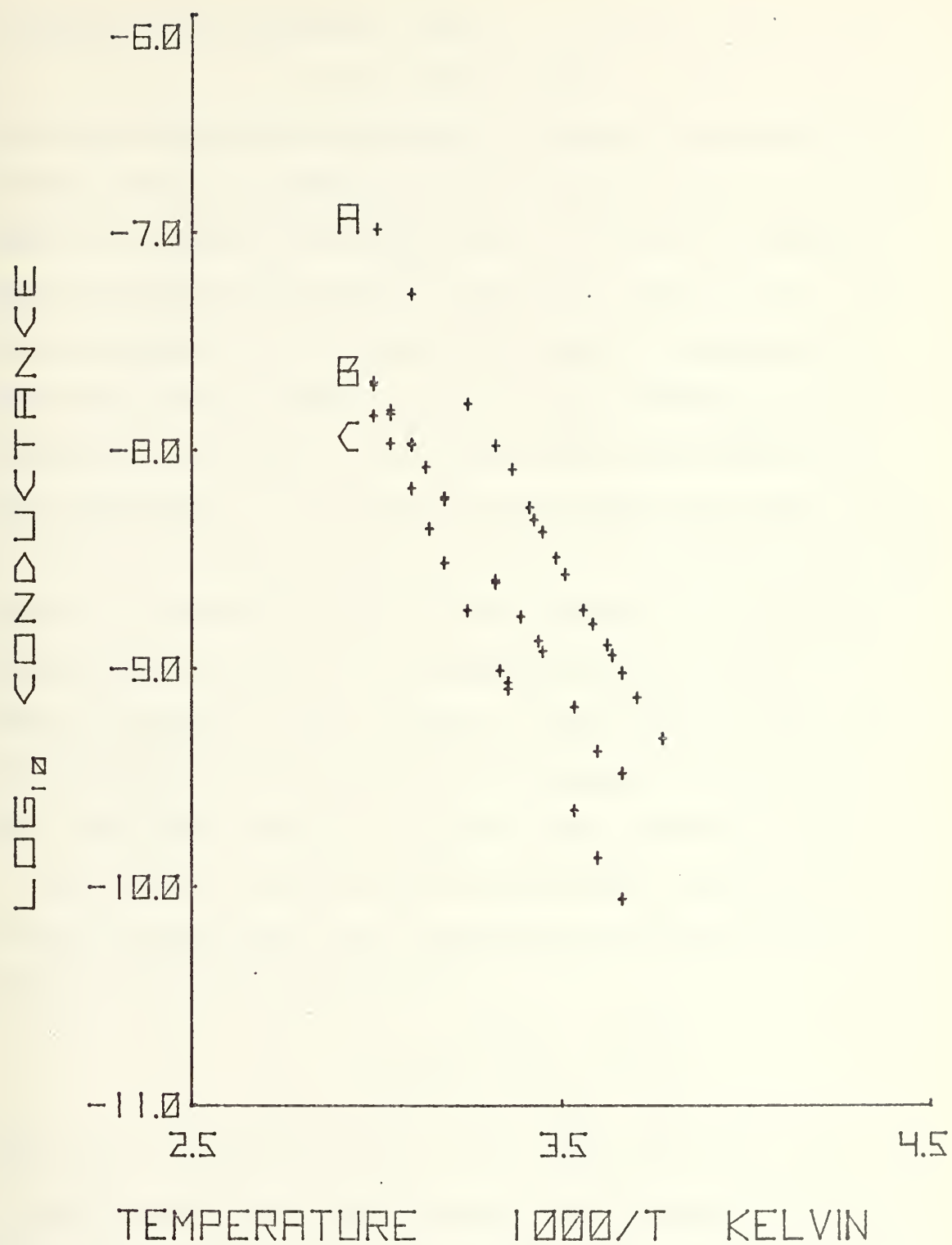


Figure 12. Conductance as function of  $1/T$ , (a) doped TCNQ  $\rho_{\perp}$ , (b) TCNQ  $\rho_{\parallel}$ , (c) TCNQ  $\rho_{\perp}$ .



activation could be determined. Since

$$\ln \sigma = \Delta E/kT + \ln \sigma_0$$

$\Delta E$  can be calculated from the slope. Even though the doped TCNQ is ten to twenty times more conductive than pure TCNQ the energy of activation appears to be the same. Pure TCNQ showed no difference in impedance when the polarity of the leads was reversed for either  $\rho_{\perp}$  or  $\rho_{\parallel}$ . The same was observed for  $\rho_{\perp}$  for doped TCNQ. However,  $\rho_{\parallel}$  measurements of doped TCNQ varied by as much as a factor of two, following reversal of the polarity of the leads. The difference became more significant at higher temperatures. The activation energy determined for these samples was found to be slightly lower for pure TCNQ than it was for orange doped TCNQ, but this difference was of the same magnitude as the accuracy of the measurements (Table III). The average activation energy for all samples is reported as  $0.55 \pm 0.08$  eV. Hiroma [Ref. 43] reports an activation energy of 0.45 to 0.60 eV for repeatedly purified TCNQ in vacuo. He achieved electrical contact by vacuum deposition of gold.

The lack of an observed doublet ESR absorption, characteristic of an excited state triplet, can be explained by the "almost-localized" electron model. The splitting term is

$$D_{xx} = (1/2)g^2\beta^2 \left\langle \frac{r_{12}^2 - 3x_{12}^2}{r_{12}^5} \right\rangle$$

[Ref. 74]. It is estimated that a value of approximately one gauss for  $D_{xx}$  would result in unresolved splitting. This corresponds to an average separation of  $18 \text{ \AA}$  needed between the DMDHT cation radical and its donated electron in the TCNQ lattice. This is consistent with a DMDHT donor having its donated electron delocalized over only a few nearby neighboring TCNQ molecules.



Chesnut and Phillips [Ref. 44] report the decomposition point of morpholinium<sup>+</sup>TCNQ<sup>-</sup>, determined by ESR appearance, as 125°C, whereas Melby [Ref. 11] reports 210°C as the decomposition point determined by normal melting point procedures. Method of preparation as well as the temperature and the length of time at the temperature affect the decomposition point of these complexes. A single doped crystal of TCNQ, affixed with stopcock grease to a quartz rod, began to show signs of decomposition at 120°C. The ESR absorption was very much broadened and underwent other irreversible changes. Concurrently, examination of the sample showed that the grease covering the crystal has become interspersed with minute blue spots. As the temperature was increased more and more blue appeared, eventually the quartz rod was stained with a blue film, apparently due to saturation of the grease. Acker [Ref. 10] reports the melting point of TCNQ as 293°-296°C and states that it can be sublimed above 250°C. Acker also notes that the glass plates used in the melting point determination turned blue due to reaction of the TCNQ<sup>-</sup> radical ion with bases in the glass.

Bulk samples examined without stopcock grease showed the same behavior as single crystals. At 100°-120°C the ESR absorption was broadened. at 140°-160°C the spectrum was still broadened, but less intense, and decrease of the signal with time was not apparent. On examination of the sample, very fine blue dust-like crystals were observed along the inside of the quartz sample tube. The blue observed in this study then, was a decomposition product and not due to a reaction with bases in glass. At 180°C the absorption became very narrow and intense. More blue deposits were noted and the doped TCNQ was noticeably lighter in color. The intensity of this narrow signal was observed to decrease with time. At





higher temperatures the decrease in intensity was accelerated. At 220°C some of the TCNQ appeared to be subliming, and some appeared to be blackening or charring. This continued until 250°C, where no other changes were observed.

Pure TCNQ had no ESR signal, and its appearance did not change until temperatures reached 160°C. At 160°C the TCNQ appeared to be beginning to sublime, and a very weak ESR absorption was noticed. Ohmasa [Ref. 45] observed the formation of solvent inclusion compounds of some TCNQ systems, however these lose their included solvent at much lower temperatures. At 180°C sublimation was marked and the ESR absorption was slightly more intense, but still 3 to 4 orders of magnitude less than the normal doped TCNQ absorption. At 220°C the small signal appeared to broaden and the TCNQ began to darken. The sublimed TCNQ was yellow as opposed to the sublimed doped TCNQ which was orange. Even at 250°C the unsublimed TCNQ had not charred as the doped TCNQ had, rather only small slightly darkened areas were noticed.

Apparently, decomposition of doped TCNQ begins at 100°-120°C but is relatively slow until 180°C. A doped TCNQ sample was heated to 185°C and its ESR was continuously observed. Initially the intensity of the ESR absorption increased markedly, by a factor of two. The temperature was kept at 185°C and the ESR absorption was monitored for 100 minutes. The linewidth increased slightly over this period but the intensity decreased to about one-half its original value. Relative intensity of the ESR absorption as a function of time is plotted in Figure 13.



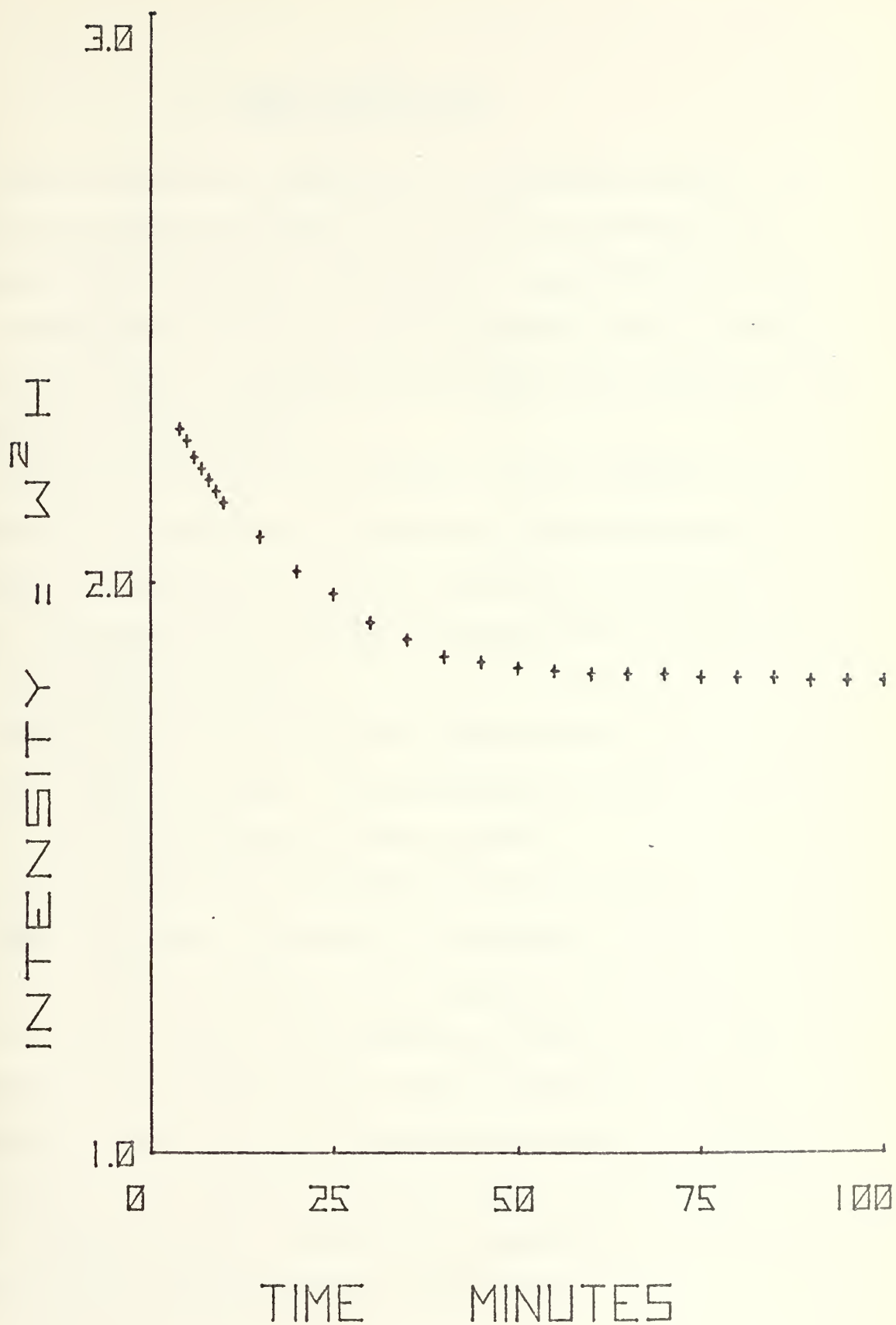


Figure 13. Data from kinetics run showing relative intensity at 185°C as a function of time.



## V. SUMMARY AND CONCLUSION

Four substituted-quinoline/TCNQ (2:1) electron donor/acceptor complexes were prepared and examined. No significant differences were observed in their ESR spectra. Bulk magnetic susceptibilities showed one, 4-methylquinolinium<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup>, to be diamagnetic. The other three, quinolinium<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup>, 2-methylquinolinium<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup>, and 7-methylquinolinium<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup> were all paramagnetic.

A complex of 1,4-dimethyl-1,4-dihydro-s-tetrazine (DMDHT) and perchlorate ion was synthesized and exhibited an intense ESR absorption. The singlet absorption had a g-value of 2.0038 and a linewidth of 2.5 gauss. The compound was not chemically analyzed and no further work with this complex was carried out.

DMDHT was also used as a donor with TCNQ, but purification of the 2:1 complex was not achieved. ESR measurements and magnetic susceptibility values were determined for impure samples.

Crystals of TCNQ doped with DMDHT resulted from attempts to produce the DMDHT/TCNQ complex. The method of first moments was used to calculate the intensity of ESR absorptions. The intensity of the ESR absorption of this sample was a constant with temperature; indicating the possibility of electrons in a conduction band. However resistivity measurements as a function of temperature indicate semiconductor nature. A possible explanation of this behavior is an excited state triplet with an activation energy of 0.02 eV. The lack of an observed ESR doublet can be explained by the "almost-localized" electron model.



DMDHT doped TCNQ crystals have a conductivity about one thousand times greater than extremely pure TCNQ. The activation energy for semi-conduction is 0.55 eV. Preliminary kinetics data indicate the presence of more than one species during decomposition of DMDHT doped TCNQ.

Based on the results obtained in this work, it appears that TCNQ has an activation energy for conduction of 0.55 eV. Apparently introduction of donor impurities of DMDHT into the TCNQ lattice produces an excited state triplet level 0.02 eV above the valence band of TCNQ. This excited state triplet level would still be approximately 0.55 eV below the TCNQ conduction band so the activation energy of conduction would remain relatively unchanged.

Additional work at lower temperatures could verify the existence of the excited state triplet. Determination of the dopant concentration and a means to vary the concentration of dopant in the TCNQ lattice would be worthwhile to further understand electron conduction in TCNQ and its complex salts.





## APPENDIX A

### Donor/Acceptor Complexes with TCNQ as Acceptor

<u>Organic Donor</u>	<u>References</u>
Quinolinium	11,49,39,48,56,57,58,47,64
5,8-Dihydroxyquinolinium	11,39
N-Methylquinolinium	11,39,48,54,56,57,58
4-Cyano-N-methylquinolinium	11,39,50,56
N-(n-Propyl)-quinolinium	11,56,58
N-Ethylquinolinium	11,54,56,57,58
N-(2-Phenethyl)-quinolinium	11,56
2-Methylquinolinium(Quinaldinium)	48,57,58
N-Methyl-2-methylquinolinium	48,57,58
N-Ethyl-2-methylquinolinium	48,54,57,58
1-Methyl-8-hydroxyquinolinium	56
Hydroquinolinium	11,56
5-Amino-8-hydroxyquinolinium	56
7,8-Benzoquinolinium	51,48,57
3,4-Benzoquinolinium	51
2,3-Benzoquinolinium	51,57
N-Methyl-3,4-benzoquinolinium	51
N-Methyl-7,8-benzoquinolinium	51,48,57
N-Methyl-2,3-benzoquinolinium	51,57
N-Ethyl-2,3-benzoquinolinium	57
Benzidinium	52
Hexamethylbenzene	51
1,5-Diaminonaphthalene	11,56
1,8-Diaminonaphthalene	11,56
2,3-Diaminonaphthalene	11,56
Anthracene	11,56
4,6,8-Trimethylazulene	11,56
Diaminodurene	11,39,56
2-Aminofluorene	11,56
2-Aminochrysene	11,56
Pyrogallol	11,56
Pyrene	11,56
Pyridinium	11,56
N-Methylpyridinium	11,56
4-Cyano-n-methylpyridinium	11
2,2'-Bipyridinium	11,47,56
2,2'-Biquinolinium	56
1,6-Diaminopyrene	55
Morpholinium	4,11,17,39,56
o-Phenylenediamine	52
p-Phenylenediamine	11,52,56
2-Methylphenylenediamine	11,56
N,N'-Dimethyl-p-phenylenediamine	11
N,N-Dimethyl-p-phenylenediamine	11,52,56
N,N-Diethyl-p-phenylenediamine	52,56



<u>Organic Donor</u>	<u>References</u>
N,N,N',N'-Tetramethyl-p-phenylenediamine	11,52,56
4-Hydroxy-2,3,5,6-tetramethylanilinium	11,56
4-Amino-N,N-diethylanilinium	11
4-Amino-2,3,5,6-tetramethylanilinium	11,47,56
4-Hydroxy-N-benzylanilinium	11
Triethylammonium	11,39,47,48,49,50,56,57
Ammonium	11,34,56
Trimethylammonium	11,39,50,56
Tetramethylammonium	34
Methyldiethylammonium	11
Methyltriethylammonium	56
Tetraethylammonium	11,34,56
t-Butyldimethylammonium	56
t-Butylammonium	56
Tetrapropylammonium	11,34,56
Isopropylammonium	56
1,11-Trimethylhydrazinium	11,56
Triethylenediamine	11
Diethylcyclohexylammonium	48,54,57
Methyldiethylcyclohexylammonium	4,48,54,57
Triethylcyclohexylammonium	4,48,57
Triphenylselenonium	11,56
Triphenylsulfonium	11,56
Tris(dimethylamino)-sulfonium	11
Trimethylphenylammonium	56
Methyltriphenylphosphonium	4,11,17,19,39,56,68
Methyltriphenylarsonium	4,11,17,19,39,50,56
Ethyltriphenylphosphonium	11,56
Ethyltriphenylarsonium	11,56
Tetraphenylstibonium	11,56,70
Tetraphenylphosphonium	11,56
N,N'-Diphenyl-p-phenylenediamine	52
N,N'-Di- $\beta$ -naphthyl-p-phenylenediamine	52
o-Phenanthroline	48,57
N-Methyl-o-phenanthroline	36,48,54,56,57
N-Ethyl-o-phenanthroline	48,57
N,N'-Dimethyl-phenazine	36
Phenazine	56
Dimethyldihydrophenazine	56
N-Methylphenazine	36,47,56,58
N-Ethylphenazine	36,56
N-Methylpyrazine	36,56
N-Methylquinoxaline	36,56
Acridinium	48,54,64
N-Methylacridinium	36,48,56,58
N-Ethylacridinium	36,48
N,N'-Dimethylacridinium	36,48
2,4,6-Triphenylpyrylium	11,39
2-(4-Dimethylaminophenyl-azo)-pyridinium	11
N-Methyl-2-(4-dimethylaminophenyl-azo)-pyridinium	11



<u>Organic Donor</u>	<u>References</u>
1,2-Benzpyrene	51
3,4-Benzpyrene	51
Ferricinium	11,56
Dimethylferricinium	11
Cobalticinium	11
Phenanthrene	59
1,2-Dimethylbenzimidazolium	4,57
1,2-Dimethyl-N-methylbenzimidazolium	4,54
1-Methylbenzimidazolium	57,61
1-Methyl-N-methylbenzimidazolium	4,54,57,61
1-Methyl-N-ethylbenzimidazolium	4,54,57,61
1,2-Dimethyl-N-ethylbenzimidazolium	57,61
Benzothiazolium	54,57,61
N-Methylbenzothiazolium	54,57,61
N-Ethylbenzothiazolium	57,61
N-Methyl-2-methylbenzothiazolium	54,57,61
2-Methyl-N-ethylbenzothiazolium	54,57,61
1-Methyl-N-ethylbenzothiazolium	54
2-Methyl-N-methylbenzoselenazolium	57,61
2-Chloropyridine	56
2-Bromopyridine	56
Nitrotriethanol	56
Diethylmethylcyanomethylammonium	56
N,N'-Pentamethylen-bis(trimethylammonium)	56
1,2-Bis(dimethylammonium)-1,2-bis(methylthio)-ethylene	56
1,2-Bis(methylthio)-1,2-dimorpholinomethylene	56
n-Octadecyltrimethylammonium	56
4-Dimethylaminoazobenzene	56,62
N-Methyl-2-styrylpyridinium	56
3,7-Diamino-2,8-dimethyl-5-phenylphenazine	56
1,4-Diazabicyclo[2.2.2]octane	56
N,N,N',N'-Tetramethylbenzidine	56,60
p-Benzylaminophenol	56
p-Dimethylaminophenol	56
N-Methyl-2-methyl-8-naphthothiazolium	57,61
Isoquinolinium	56
N-Methylisoquinolinium	58
N-Ethylisoquinolinium	58
4-Methylquinolinium	58
N-Methyl-4-methylquinolinium	58
N-Ethyl-2,6-dimethylquinolinium	58
Tetrabutylammonium	34
Tetrapentylammonium	34
Tetrahexylammonium	34
Carbazole	59
Fluorene	59
Dibenzene thiophene	59
Dibenzofuran	59
Benzidine	60
o-Tolidine	60



<u>Organic Donor</u>	<u>References</u>
o,o'-Dibromo-o-tolidine	60
o,o'-Dichloro-o-tolidine	60
2,3-Dimethylbenzimidazolium	61
2,3-Dimethyl-N-methylbenzimidazolium	61
2,3-Dimethyl-N-ethylbenzimidazolium	61
4-Aminoazobenzene	62
3'-Nitro-4-dimethylaminoazobenzene	62
4'-Nitro-4-dimethylaminoazobenzene	62
4'-Nitro-4-diethylaminoazobenzene	62
3'-Methylmercapto-4-dimethylaminoazobenzene	62
4'-Methyl-4-dimethylaminoazobenzene	62
4'-Fluoro-4-dimethylaminoazobenzene	62
3'-Methyl-4-dimethylaminoazobenzene	62
2'-Methylmercapto-4-dimethylaminoazobenzene	62
2'-Methyl-4-dimethylaminoazobenzene	62
4'-Methylmercapto-4-dimethylaminoazobenzene	62
4-Diethylaminoazobenzene	62
3'-Methyl-4-diethylaminoazobenzene	62
4'-Methoxy-4-dimethylaminoazobenzene	62
4'-Fluoro-4-diethylaminoazobenzene	62
4'-Ethyl-4-diethylaminoazobenzene	62
Thiazolinocarbocyanine	64
3,3'-Diethyl-2,2'-thiazolinocarbocyanine	63
1,2-Bis(4-pyridyl)ethane	65
1,2-Bis(4-pyridyl)ethylene	65
N,N'-Dihydro-4,4'-bipyridinium	67
N,N'-Dimethyl-4,4'-bipyridinium	67
p-Aminobenzenesulfonamide	68
Sulfaguanidine	68
Biphenylene	66
Stilbene	66
Tolane	66
9,10-Anthroquinone	66
1,4-Naphthaquinone	66
Pyridine	69
$\beta$ -Picoline	69
Piperidine	71
Pyrrolidine	71
Tetrathiotetracene	5,71
Phenothiazines	73
N-Ethylcarbozole	72
7-Methyl-6H-[1]benzopyrano[4.3-b]quinolinium	70
11-Methyl-9-phenyl-7,8,9,10-tetrahydro-6H-cyclohepta[b]quinolinium	70
13-Methyl-6,7-dihydro-5H-benzo[3.4]cyclohepta[1.2-b]quinolinium	70
20-Methyl-6,7,8,9,10,11,12,13,14,15,16,17,18,19-tetradecahydrodicyclohexadeca[b]quinolinium	70
2-Benzyl-4-methyl-3-phenylquinolinium	70
5,9-Dimethyl-7,8-dihydro-6H-cyclopenta[b]quinolinium	70
5,10-Dimethyl-6,7,8,9-tetrahydrobenzo[b]quinolinium	70
3,3'-Diethylthiacyanine	63
5-[2-(-Ethyl-2-benzoxazolinylidene)-ethylidene]-3-ethylrhodamine	63







<u>Organic Donor</u>	<u>References</u>
7-Chlorotetracycline	68
1-Methyl-3-hydroxy-piperidene	71
1-Methyl-piperidene	71
1-Methyl-3-piperidylbis(2-thienyl)methane	71
1-(1-Methyl-2-pyrrolidyl)-3-propanol	71
1-(1-Dimethylamino-2-cyclopentyl)-2,5-pentanediol	71

<u>Metal/Metal Complex Donors</u>	<u>References</u>
$\text{Li}^+$	4,11,39,56
$\text{Na}^+$	11,39,56
$\text{K}^+$	11,39,49,50,56
$\text{Cs}^+$	11,39,56
$(\text{Cs}^+)_2$	4,11,17,19,39,50
$\text{Ba}^+$	11,39,56
$\text{Mn}^{++}$	11,39,56
$\text{Fe}^{++}$	11,39
$\text{Co}^{++}$	11,56
$\text{Ni}^{++}$	11,39
$\text{Cu}^+$	11,39
$\text{Cu}^{++}$	11,39
$\text{Ag}^+$	11,39
$\text{Ce}^{+++}$	11
$\text{Sm}^{+++}$	11
$\text{Pb}^{++}$	11
$\text{Cu}(\text{NH}_3)_2^{++}$	11
$\text{Cu}(\text{NCH}_2\text{CH}_2\text{NH}_2)_2^{++}$	11
$\text{Cu}(2,2'\text{-dipyridylamine})^{++}$	11
$\text{Mn}(1,10\text{-phenanthroline})_3^{++}$	11,56
$\text{Fe}(1,10\text{-phenanthroline})_3^{++}$	11,56
$\text{Cu}(1,10\text{-phenanthroline})_3^{++}$	56
$\text{Ni}(1,10\text{-phenanthroline})_3^{++}$	11
$\text{Co}(1,10\text{-phenanthroline})_3^{++}$	56
$\text{Ni}(1,10\text{-phenanthroline})_2^{++}$	11



<u>Metal/Metal Complex Donors</u>	<u>References</u>
Ni(2,2'-bipyridene) <sub>3</sub> <sup>++</sup>	56
Rb <sup>+</sup>	4
Cu-8-quinolate	11,56
Cu chelate of pyrrole-2-aldehydeimine	11,56
Ni chelate of pyrrole-2-aldehydeimine	11,56

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## BIBLIOGRAPHY

1. Schlenk, W., Ann., v. 368, p. 277, 1909.
2. Mulliken, R. S., "Molecular Compounds and Their Spectra. II," Journal of the American Chemical Society, v. 74, p. 811-824, 1952.
3. Brenig, W., Dohler, G. H., Heyszenau, H., " $T^{-1/3}$ -Hopping in Organic Charge Transfer Crystals?," Physics Letters, v. 39A, p. 175-176, 1972.
4. Hibma, T., Dupuis, P., Kommandeur, J., "Excitons In TCNQ-Salts," Chemical Physics Letters, v. 15, p. 17-20, 1972.
5. Perez-Albuerné, E. A., Johnson, H., Trevoy, D. J., "Highly Conducting Ion-Radical Salts of Tetrathietetracene," The Journal of Chemical Physics, v. 55, p. 1547-1554, 1971.
6. Bijl, D., Kainer, H., Rose-Innes, A. C., "Biradical Molecular Compounds: A Study by Electron Spin Resonance," The Journal of Chemical Physics, v. 30, p. 765-770, 1959.
7. Akamatu, H., Inokuchi, H., Matsunga, Y., "Organic Semi-conductors with High Conductivity. I. Complexes Between Polycyclic Aromatic Hydrocarbons and Halogens," The Bulletin of the Chemical Society of Japan, v. 29, p. 213-220, 1956.
8. Kommandeur, J., Hill, F. R., "Low Resistance Organic Semi-conductor," Bulletin of the American Physics Society, Series II, v. 4, p. 421-428, 1959.
9. Acker, D. S., et al, "7,7,8,8-Tetracyanoquinodimethane and its Electrically Conducting Anion-Radical Derivatives," Journal of the American Chemical Society, v. 82, p. 6408-6409, 1960.
10. Acker, D. S., Hertler, W. R., "Substituted Quinodimethans. I. Preparation and Chemistry of 7,7,8,8-Tetracyanoquinodimethan," Journal of the American Chemical Society, v. 84, p. 3370-3374, 1962.
11. Melby, L. R., et al, "Substituted Quinodimethans. II. Anion-Radical Derivatives and Complexes of 7,7,8,8-Tetracyanoquinodimethan," Journal of the American Chemical Society, v. 84, p. 3374-3387, 1962.
12. Farges, J. P., Brau, A., Gutmann, F., "Electrical Conductivity of Single Crystals of Triethylammonium-(TCNQ)<sub>2</sub>," Journal of the Physical Chemistry of Solids, v. 33, p. 1723-1726, 1972.
13. Suezaki, Y., "On the Magnetic Properties of TCNQ Anion Radical Salts-(2)," Physics Letters, v. 40A, p. 419-420, 1972.



14. Ferraris, J., et al, "Electron Transfer In a New Highly Conducting Donor-Acceptor Complex," Journal of the American Chemical Society, v. 95, p. 948-949, 1973.
15. McConnell, H. M., Lynden-Bell, R., "Paramagnetic Excitons in Solid Free Radicals," The Journal of Chemical Physics, v. 36, p. 2393-2397, 1962.
16. McConnell, H. M., Griffith, H. O., Pooley, D., "Spin Exchange Between Excitons and Free Radicals," v. 36, p. 2518-2519, 1962.
17. Jones, M. T., Chesnut, D. B., "Triplet Spin Exchange in Some Ion Radical Salts," The Journal of Chemical Physics, v. 38, p. 1311-1317, 1963.
18. Chesnut, D. B., "Simple Model for Some Dense Magnetic Exciton Systems," The Journal of Chemical Physics, v. 40, p. 405-411, 1964.
19. Jones, M. T., "Spin-Lattice Relaxation in Some TCNQ Ion-Radical Salts," The Journal of Chemical Physics, v. 40, p. 1837-1842, 1964.
20. Chesnut, D. B., "Phonon-Induced Exciton Interactions," The Journal of Chemical Physics, v. 41, p. 472-474, 1964.
21. Maréchal, M. A., McConnell, H. M., "Triplet Excitons in Morpholinium TCNQ," The Journal of Chemical Physics, v. 43, p. 497-498, 1965.
22. Soos, Z. G., Hughes, R. C., "Paramagnetic Susceptibilities and Temperature-Dependent Excitation Energies in Linear Organic Crystals," The Journal of Chemical Physics, v. 46, p. 253-259, 1967.
23. Ohmura, M., Kinoshita, M., Akamatsu, H., "Mechanochemical Spin Generation in a Solid Charge-Transfer Complex," Bulletin of the Chemical Society of Japan, v. 42, p. 2402-2403, 1969.
24. Epstein, A. J., et al, "Metal-Insulator Transition and Antiferromagnetism in a One-Dimensional Organic Solid," Physical Review B, v. 5, p. 952-977, 1972.
25. Hertler, W. R., et al, "Substituted Quinodimethanes. III. Displacement Reactions of 7,7,8,8-Tetracyanoquinodimethan," Journal of the American Chemical Society, v. 84, p. 3387-3393, 1962.
26. Hertler, W. R., Benson, R. E., "Substituted Quinodimethanes. IV. 7,7,8,8-Tetrakis-(ethylsulfonyl)-quinodimethan," Journal of the American Chemical Society, v. 84, p. 3474-3478, 1962.
27. Williams, J. K., "Substituted Quinodimethanes. V. p-Tricyanovinylphenyldicyanomethide and Related Anions," Journal of the American Chemical Society, v. 84, p. 3478-3479, 1962.





28. Diekmann, J., Hertler, W. R., Benson, R. E., "Substituted Quinodimethans. VII. Substituent and Structural Effects in Cyano-Substituted Quinodimethans," Journal of Organic Chemistry, v. 28, p. 2719-2724, 1963.
29. Tolles, W. M., McBride, W. R., Thun, W. W., "An Electron Spin Resonance Study of Several 1,4-dihydro-s-tetrazine Cation Radicals," Journal of the American Chemical Society, v. 91, p. 2443-2446, 1969.
30. Sundaresan, T., Wallwork, S. C., "The Crystal Structures of Free Radical Salts and Complexes. II. (N-(n-Propyl)quinolinium)<sup>+</sup>(7,7,8,8-Tetracyanoquinodimethane)<sub>2</sub><sup>-</sup>," Acta Crystallographica, Section B, v. 28, p. 1163-1169, 1972.
31. Sundaresan, T., Wallwork, S. C., "The Crystal Structures of Free Radical Salts and Complexes. III. (N,N'-Dibenzyl-4,4'-bipyridylum)<sup>2+</sup>-(7,7,8,8-Tetracyanoquinodimethane)<sub>2</sub><sup>-</sup>," Acta Crystallographica, Section B, v. 28, p. 2474-2480, 1972.
32. Fritchie, C. J., Arthur, P., "A Refinement of the Crystal Structure of Cesium Tetracyanoquinodimethanide," Acta Crystallographica, v. 21, p. 139-145, 1966.
33. Berlinotti, F., et al, "The Structure of Heterocyclis Compounds Containing Nitrogen. I. Crystal and Molecular Structure of s-Tetrazine," Acta Crystallographica, v. 9, p. 510-514, 1956.
34. Kusakawa, H., Akashi, K., "Space Effects of Tetra-n-alkyl Ammonium Ions on the Electrical Conduction of Tetracyanoquinodimethane Salts," Bulletin of the Chemical Society of Japan, v. 42, p. 263-265, 1969.
35. Matsunaga, Y., "The Size and Shape of the Component Molecules as the Factors Determining the Electronic Structure of Crystal Complexes," Bulletin of the Chemical Society of Japan, v. 42, p. 2490-2493, 1969.
36. Melby, L. R., "Substituted Quinodimethans, VIII. Salts Derived From the 7,7,8,8-Tetracyanoquinodimethan Anion-Radical and Benzologues of Quaternary Pyrazinium Cations," Canadian Journal of Chemistry, v. 43, p. 1448-1453.
37. Assenheim, H. M., Introduction to Electron Spin Resonance, p. 70, Plenum Press, 1967.
38. Kneubühl, F. K., "Line Shapes of Electron Paramagnetic Resonance Signals Produced by Powders, Glasses, and Viscous Liquids," Journal of Chemical Physics, v. 33, p. 1074-1079, 1960.
39. Siemons, W. J., Bierstedt, P. E., Kepler, R. G., "Electronic Properties of a New Class of Highly Conductive Organic Solids," Journal of Chemical Physics, v. 39, p. 3523-3528, 1963.
40. Chesnut, D. B., Foster, H., Phillips, W. D., "EPR Studies of Spin Correlation in Some Ion Radical Salts," Journal of Chemical Physics, v. 34, p. 684-685, 1961.



41. Chesnut, D. B., Arthur, P., "Spin Correlation in Ion Radical Salts; The System  $(\text{Cs}^+)_2(\text{TCNQ})_3^-$ ," Journal of Chemical Physics, v. 36, p. 2967-2975, 1962.
42. Kittel, C., Introduction to Solid State Physics, 4th ed., Wiley, p. 518-520, 1971.
43. Hiroma, S., Kuroda, H., Akamatsu, H., "Semiconductivity and Photoconductivity of TCNQ Crystal," Bulletin of the Chemical Society of Japan, v. 44, p. 974-977, 1971.
44. Chesnut, D. B., Phillips, W. D., "EPR studies of Spin Correlation in Some Ion Radical Salts," Journal of Chemical Physics, v. 35, p. 1002-1012, 1961.
45. Ohmura, M., Kinoshita, M., Akamatsu, H., "Inclusion Compounds of Some Charge Transfer Complexes," Bulletin of the Chemical Society of Japan, v. 44, p. 391-396, 1971.
46. Tsien, R. W., Huggins, C. M., BeBlanc, O. H., "Electron Spin Resonance in Quinolinium(TCNQ)<sub>2</sub>: An Organic Semimetal," Journal of Chemical Physics, v. 45, p. 4370-4371, 1966.
47. Siratori, K., Kondow, T., "Magnetic Susceptibilities of TCNQ Complexes," Journal of the Physical Society of Japan, v. 27, p. 301-306, 1969.
48. Dupuis, P., Néel, J., "Conductivité électrique de quelques complexes du tétracyanoquinodiméthane," C. R. Acad. Sc. Paris, t. 265, p. 688-690, 1967.
49. Kepler, R. G., Bierstedt, P. E., Merrifield, R. E., "Electronic Conduction and Exchange Interaction in a New Class of Conductive Organic Solids," Physical Review Letters, v. 5, p. 503-504, 1960.
50. Kepler, R. G., "Magnetic Properties of a New Class of Highly Conductive Organic Solids," Journal of Chemical Physics, v. 39, p. 3528-3552, 1963.
51. Slough, W., "Electron Spin Resonance and Absorption Spectra of Some Semiconductor  $\pi$ -Complexes and Electron Transfer Salts of Tetracyanoquinodimethane," Transactions of the Faraday Society, v. 61, p. 408-414, 1965.
52. Ohmura, M., et al, "Electronic Properties of Some Complexes of Tetracyanoquinodimethane with Aromatic Diamines," Bulletin of the Chemical Society of Japan, v. 41, p. 1998-2004, 1968.
53. Sano, H., et al, "Spin Correlation in Metal-Chelate TCNQ Radical Salts," Bulletin of the Chemical Society of Japan, v. 41, 2204-2204, 1968.



54. Dupuis, P., Flandrois, S., Néel, J., "Propriétés magnétiques de quelques nouveaux complexes du tétracyanoquinodiméthane," C. R. Acad. Sc. Paris, t. 269, p. 1091-1094, 1969.
55. Scott, H., et al, "Conductive Salt of the Radical Cation of 1,6-Diaminopyrene and the Radical Anion of 7,7,8,8-Tetracyanoquinodimethane," Journal of Physical Chemistry, v. 69, p. 1740-1742, 1965.
56. Acker, D. S., Blomstrom, D. C., Charge Transfer Compounds of 7,7,8,8-Tetracyanoquinodimethan and C-hydrocarbonyl Substituted 7,7,8,8-Tetracyanoquinodimethans with Lewis Bases, U. S. Patent 3,162,641, 22 December 1964.
57. Buvet, R., et al, "Préparation et étude des associations salines qui se forment entre les cations ammonium quaternaires organiques et l'anion-radical obtenu par réduction du tétracyanoquinodiméthane," Bulletin de la Société Chimique de France, v. 11, p. 3991-4000, 1969.
58. Iida, Y., "Electronic Spectra of Crystalline TCNQ Anion Radical Salts. II. Complex Salts," Bulletin of the Chemical Society of Japan, v. 42, p. 637-643, 1969.
59. Mukherjee, T. K., "Charge-Transfer Donor Abilities of o,o'-Bridged Biphenyls," Journal of Physical Chemistry, v. 73, p. 3442-3445, 1969.
60. Matsunaga, Y., Saito, G., "Electronic Spectra and Electrical Resistivities of the Molecular Complexes of Benzidine and Its Derivatives," Bulletin of the Chemical Society of Japan, v. 44, p. 958-963, 1971.
61. Dupuis, P., Néel, J., "Conductivité électrique de quelques nouveaux complexes du tétracyanoquinodiméthane," C. R. Acad. Sc. Paris, t. 265, p. 777-779, 1967.
62. Damerau, W., "Charge Transfer-Komplexe von Aminoazofarbstoffen mit Tetracyanchinondimethan," Z. Naturforsch., v. 31 b, p. 937-939, 1966.
63. Yagubskii, E. B., et al, "Potential Organic Superconductors. I. Complexes of Dyes with 7,7,8,8-Tetracyanoquinodimethan," Zh. Obshch. Khim., v. 38, p. 992-998, 1968.
64. Buravov, L. I., Fedutin, D. N., Shchegolev, I. F., "Conduction Mechanism in Highly Conductive Complexes Based on Tetracyanoquinodimethan," Zh. Eksp. Teor. Fiz., v. 59, p. 1125-1132, 1970.
65. Rembaum, A., et al, "Electronic Properties of Some Tetracyanoquinodimethan Complexes," Journal of Physical Chemistry, v. 73, p. 513-520, 1969.
66. Pécile, C., Lunelli, B., "Vibrational Spectra of Molecular Crystals," Corsi Semin. Chim., v. 19, p. 53-56, 1969.
67. Rembaum, A., Hadek, V., Yen, S. P. S., "Electron Transfer to Bipyridinium(Paraquat) Salts," Journal of the American Chemical Society, v. 93, p. 2532-2534, 1971.





68. Alikin, A. A., et al, "Excited States in Complexes of Tetracyanoquinodimethan with Various Donors," Opt. Spektresk., v. 31, p. 249-251, 1971.
69. Markova, N. A., Orlev, I. G., Zaikev, G. E., "Reaction of 7,7,8,8-Tetracyanoquinodimethan with Polymers and Monomers of the Pyridine Series in Solutions," Izv. Akad. Nauk SSSR, Ser. Khim., v. 1970, p. 1051-1055, 1970.
70. Heinning, D., Kempter, G., "Electron Donor-Acceptor Complexes of Elementary Organic Compounds of Group V of the Periodic System. III. Complexes of Organic Antimony and Nitrogen Derivatives with Tetracyanoquinodimethan," Z. Chem., v. 10, p. 343-344, 1970.
71. Khidekel, M. L., et al, "Complex Salts of Some Hydroxy and Halo Derivatives of Piperidine and Pyrrolidine with 7,7,7,8-Tetracyanoquinodimethan," Izv. Akad. Nauk SSSR. Ser. Khim., v. 1972, p. 450-455, 1972.
72. Rembaum, A., Hermann, A. M., Haack, R., "Charge Transfer Complexes of N-Ethylcarbazole and poly(N-vinylcarbazole)," Journal of Polymer Science, Part A-1, v. 6, p. 1955-1963, 1968.
73. Fulton, A., "Absorption Spectra of the Anions of Quinones and Other Acceptors in Solution and as Solids," Australian Journal of Chemistry, v. 21, p. 2847-2852, 1968.
74. Carrington, A., McLachlan, A. D., Introduction to Magnetic Resonance, p. 116-118, Harper-Row, 1967.





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Stefan Alan Nyarady

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13. ABSTRACT

Complex 2:1 TCNQ salts of quinoline, 2-methylquinoline, 4-methylquinoline, and 7-methylquinoline were made. Their ESR spectra were observed and their magnetic susceptibilities and resistivities were determined. A new donor, 1,4-dimethyl-1,4-dihydro-s-tetrazine(DMDHT), was tried with TCNQ as acceptor. Magnetic susceptibility, resistivity, and ESR g-value measurements were made on the resulting complex. A complex of  $\text{DMDHT}^+/\text{ClO}_4^-$  was made and an intense ESR singlet was observed.

TCNQ crystals doped with DMDHT resulted from attempts to make the  $\text{DMDHT}^+(\text{TCNQ})_2^-$  complex salt. Resistivity measurements showed these crystals to be  $10^3$  times more conducting than extremely pure TCNQ. Variable temperature studies showed an activation energy for conduction of 0.55 eV for both the doped and undoped TCNQ.

The ESR absorption of doped TCNQ was relatively constant from 350°K to 100°K. A possible explanation for this observed behavior is an excited state triplet 0.02 eV above the valence band of TCNQ. The lack of an observed doublet is explained with the "almost-localized" electron model.

As ESR kinetic study of the high temperature decomposition of TCNQ indicated more than one species resulting from decomposition.



## KEY WORDS

## LINK A

## LINK B

## LINK C

ROLE

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7,7,8,8-Tetracyanoquinodimethane

TCNQ

Organic Semiconductor

Charge Transfer Complex

Electron paramagnetic resonance

Doped TCNQ

Donor/TCNQ (2:1) complex salts



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